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### Electrochemical CO<sub>2</sub> reduction by a cobalt bipyricorrole complex: decrease of an overpotential value derived from monoanionic ligand character of the porphyrinoid species<sup>†</sup>

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A newly synthesized Co(II) complex with a monoanionic bipyricorrole ligand is found to catalytically promote a selective  $CO_2$  electroreduction to CO with Faradaic efficiency of 75%. Catalytic Tafel plots show that the overpotential of Co(II) bipyricorrole is 0.35 V lower than that of a Co(II) complex with the dianionic tetraphenylporphyrin ligand.

Provision of effective conversion of carbon dioxide (CO<sub>2</sub>) into various compounds including fuels and chemical materials by electrocatalysis has been recognized as one of the most important objectives for realization of an environmentally sustainable society.<sup>1</sup> Over the last three decades, a wide variety of homogenous metal complexes based on first-row transition metals such as Mn,<sup>2</sup> Fe,<sup>3</sup> Co<sup>4</sup> and Ni<sup>5</sup> have been reported as useful and practical CO<sub>2</sub> reduction electrocatalysts because they are relatively inexpensive and abundant. Porphyrin (Chart 1a) is a promising catalyst ligand because it has intrinsically high durability and excellent photochemical and electrochemical properties. Iron porphyrin complexes have been extensively studied and are highly effective in converting CO2 into carbon monoxide (CO).6 In contrast, investigations of cobalt porphyrin complexes have been quite limited despite their potential as CO<sub>2</sub> reduction catalysts.<sup>7</sup> Although cobalt complexes formed by other porphyrinoids such as phthalocyanine<sup>8</sup> and corrole<sup>9</sup> have been investigated as CO<sub>2</sub> reduction catalysts, a

significantly negative electrochemical potential to generate an active low-valent intermediate is required. In this context, it is important to promote the generation of the low-valent species by tuning the ligand structure. Corrin (Chart 1b), a monoanionic porphyrinoid ligand, is the natural cofactor of cobalamin. This ligand stabilizes the low-valent species to induce formation of the Co(I) species, which serves as a key intermediate for a broad range of reactions in biological systems.<sup>10</sup> The tetradehydrocorrin derivatives shown in Chart 1c have been synthesized as simple analogs of cobalamin and physicochemical properties of their cobalt complexes have been previously investigated.<sup>11</sup> Our recent study, however, has demonstrated that a stabilized Co(1) species with a tetradehydrocorrin framework as a ligand promotes selective  $H_2$  evolution rather than  $CO_2$  reduction.<sup>12</sup> Thus, we hypothesize that suitable stabilization of the Co(1) species will be required to promote a selective CO<sub>2</sub> reduction reaction with a low overpotential value. Here, we employ a bipyricorrole framework (Chart 1d),<sup>13</sup> because the stronger Lewis basicity of the nitrogen atoms in a bipyridine moiety of bipyricorrole relative to the corresponding imine-like nitrogen atoms in the bipyrrolic moiety of tetradehydrocorrin promises a more reactive Co(1) species in this metal complex. Therefore, we have designed and investigated a Co(II) bipyricorrole (Co(II)BIPC) functionalized with a 2,6-dimethoxyphenyl group at a meso-position of the bipyricorrole framework (Scheme 1).<sup>14</sup>

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Chart 1 Deprotonated structures of (a) porphyrin, (b) corrin, (c) tetradehydrocorrin and (d) bipyricorrole frameworks.

 $<sup>\</sup>dagger$  Electronic supplementary information (ESI) available. CCDC 1876629. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c8cc08876d



Scheme 1 Synthesis of Co(II)BIPC. (a) 2,6-Dimethoxybenzaldehyde, HCl, H<sub>2</sub>O, ethanol, 51%; (b) NaOH, ethanol, 81%; (c) <sup>n</sup>BuLi, CuCl<sub>2</sub>, diethyl ether, 24%; (d) <sup>n</sup>BuLi, DMF, THF, 41%; (e) trifluoroacetic acid, THF (f) Co(OAc)<sub>2</sub>·4H<sub>2</sub>O, CH<sub>3</sub>OH, CH<sub>2</sub>Cl<sub>2</sub>, then NaClO<sub>4</sub>·H<sub>2</sub>O, H<sub>2</sub>O, CH<sub>3</sub>OH, 25% in 2 steps.

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**Co**(**n**)**BIPC** was successfully synthesized according to Scheme 1 (see Scheme S1, ESI,<sup>†</sup> for details). The target complex was achieved *via* acid-catalyzed intermolecular coupling of corresponding 5,5'-dicarboxydipyrromethane and 6,6'-diformyl-2,2'-bipyridine followed by cobalt insertion in a 25% yield. The zinc analog (**Zn**(**n**)**BIPC**) was also synthesized as a reference compound according to Scheme S1, ESI,<sup>†</sup> **Zn**(**n**)**BIPC** was fully characterized by NMR spectroscopy (Fig. S9 and S10, ESI<sup>†</sup>), in contrast to **Co**(**n**)**BIPC** which shows paramagnetic Co(**n**) behavior (*vide infra*).

The structure of Co(n)BIPC was determined by X-ray crystallographic analysis. In the crystal, the macrocycle of bipyricorrole is nearly planar and the coordination site of the cobalt ion is open to allow entry of external substrates as shown in Fig. 1. An aryl moiety linked to the C11 atom is close to being perpendicular to the macrocycle, indicating that the methoxy substituents in the aryl group are positioned to interact with the external substrate bound to the cobalt ion in the framework, in an arrangement which is similar to a Mn-based complex described in a previous report by Rochford.<sup>15</sup>

Cyclic voltammetry (CV) of Co(II)BIPC in a DMF solution under an N<sub>2</sub> atmosphere displays two reversible peaks with  $E_{1/2}$ of -0.87 V and -1.75 V (Fig. 2a).<sup>16</sup> The first reduction event at -0.87 V was confirmed by EPR experiments to represent cobaltbased reduction of Co(II)BIPC to form Co(I)BIPC (Fig. S13, ESI<sup>+</sup>). Eight hyperfine peaks can be seen in Fig. S13a (ESI<sup>†</sup>) due to the interaction with the Co nucleus (I = 7/2) with  $g_{\parallel} = 1.99$ , supporting the presence of a Co(II) species with the unpaired electron of the Co atom in a low-spin d<sup>7</sup> configuration. Upon addition of an excess amount of NaBH4 as a one-electron reductant, the signals derived from the  $Co(\pi)$  species completely disappear (Fig. S13b, ESI<sup>+</sup>), suggesting the formation of the Co(1) species. The absorption change corresponding to [Co(II)BIPC]/ [Co(1)BIPC] was also monitored using cobaltocene as a oneelectron reductant, which has a reduction potential of -1.3 V (Fig. S14, ESI<sup>†</sup>). Furthermore, the absence of the redox peak at -0.87 V in the CV measurement of Zn( $\pi$ )BIPC rules out a ligandbased reduction at the first reduction of Co(II)BIPC, whereas the presence of the redox peak at -1.75 V of Zn(II)BIPC indicates that the second reduction of  $Co(\pi)BIPC$  is attributed to the ligand-based reduction (Fig. S15, ESI<sup> $\dagger$ </sup>). Compared to a Co( $\pi$ )



**Fig. 1** X-ray crystal structure of **Co(II)BIPC** with 50% thermal ellipsoid probability. (a) Top view and (b) side view. Hydrogen atoms and the nonbonding counter anion ( $ClO_4^-$ ) are omitted for clarity. Only the major configuration of the disordered groups is shown. Methanol as a neutral axial ligand in the top view and an aryl group in the side view are also omitted for clarity.



Fig. 2 (a) CV of  $Co(\iota)BIPC$  (0.5 mM) in dry DMF with 0.1 M TBAPF<sub>6</sub> under an N<sub>2</sub> atmosphere. (b) CVs of  $Co(\iota)BIPC$  (0.5 mM) in dry DMF containing 0.1 M TBAPF<sub>6</sub> under N<sub>2</sub> (black) and CO<sub>2</sub> with various concentrations of H<sub>2</sub>O (from blue to purple): [H<sub>2</sub>O] = 0, 1, 2, 3, 4, and 5 M. Scan rate: 100 mV s<sup>-1</sup>.

complex of dianionic tetraphenylporphyrin (Co(II)TPP,  $E_{1/2}$ (Co<sup>II/I</sup>) = -1.28 V, Fig. S25, ESI<sup>†</sup>), the first redox potential of Co(II)BIPC is positively shifted by 0.41 V because of the significant stabilization of the Co(I) species by the monoanionic bipyricorrole ligand.

The CV trace of  $Co(\pi)BIPC$  measured under a  $CO_2$  atmosphere exhibits a significant current enhancement after the second reduction process (Fig. 2b, blue profile). Addition of H<sub>2</sub>O as a proton source results in a continuous increase in current at -2.17 V and the catalytic current reaches saturation with 5 M H<sub>2</sub>O (Fig. 2b and Fig. S16, ESI<sup>†</sup>). The catalytic current was not observed upon addition of H2O under an N2 atmosphere (Fig. S17, ESI<sup>†</sup>). To determine the reaction corresponding to the current enhancement in the CV measurements, controlledpotential electrolysis (CPE) experiments for Co(II)BIPC were conducted at a potential of -2.17 V for 1 h in a CO<sub>2</sub>-saturated DMF solution containing 5 M H<sub>2</sub>O. Analysis of the gas phase by gas chromatography revealed selective CO production with Faradaic efficiency (FE) of 75%, whereas FE of a competing  $H_2$ evolution was found to be 6% (Table 1, entry 1). Formic acid in the liquid phase was not detected by ion chromatography. A rinse test performed after the CPE demonstrated negligible

Table 1 Electrochemical data for Co(II)BIPC

Atm.	Additive	FE (CO)/FE $(H_2)^a$	$i_{\rm cat}/i_{\rm p}{}^b$	$k_{ m obs}{}^c  ({ m s}^{-1})$
$CO_2$	5 M H <sub>2</sub> O	75/6	6.3	7.8
$CO_2$	5 M TFE	77/6	_	_
$N_2$	9.0% v/v buffer	0/84	3.9	3.0
	Atm. CO <sub>2</sub> CO <sub>2</sub> N <sub>2</sub>	Atm.Additive $CO_2$ 5 M H_2O $CO_2$ 5 M TFE $N_2$ 9.0% v/v buffer	Atm.         Additive         FE $(CO)/FE (H_2)^a$ CO <sub>2</sub> 5 M H <sub>2</sub> O         75/6           CO <sub>2</sub> 5 M TFE         77/6           N <sub>2</sub> 9.0% v/v buffer         0/84	Atm.         Additive         FE (CO)/FE (H <sub>2</sub> ) <sup>a</sup> $i_{cat}/i_p^{b}$ CO <sub>2</sub> 5 M H <sub>2</sub> O         75/6         6.3           CO <sub>2</sub> 5 M TFE         77/6            N <sub>2</sub> 9.0% v/v buffer         0/84         3.9

<sup>*a*</sup> CPE experiments in entries 1 and 3 were performed at -2.17 V and CPE in entry 2 was conducted at -2.28 V. <sup>*b*</sup> Calculated at -2.17 V. <sup>*c*</sup> Determined as an apparent rate constant at -2.17 V at a scan rate of 100 mV s<sup>-1</sup> using the equation in ref. 3*a* (see ESI for details).

enhancement of the current compared to a fresh working electrode (Fig. S18, ESI†). This indicates that the catalytic performance is not derived from an electrodeposition on the electrode. The UV-vis spectra of an aliquot of the electrochemical solution before and after the CPE experiments show that nearly 90% of the complex is maintained after 1 h of CPE, indicating that **Co**(**u**)**BIPC** has high durability in electrocatalysis (Fig. S19, ESI†). The alternative proton source 2,2,2-trifluoroethanol (TFE) was also investigated. Upon addition of TFE under a CO<sub>2</sub> atmosphere, current enhancement was observed in the CV measurement, which reached a maximum when 5 M TFE was added (Fig. S20, ESI†). The CPE experiment conducted at -2.28 V in CO<sub>2</sub>-saturated DMF with 5 M TFE revealed that the enhanced current in the CV measurement corresponds to a CO<sub>2</sub>-to-CO reduction with FE of 77% along with the competing H<sub>2</sub> evolution with FE of 6% (Table 1, entry 2).<sup>17</sup>

To investigate the competing  $H_2$  evolution catalyzed by Co(n)BIPC in the presence of  $H_2O$  under a  $CO_2$  atmosphere, pseudo-pH regulation experiments were conducted under  $CO_2$ -free conditions using a buffer solution containing a mixture of 15 mM each of MES, TAPS, HEPES and CHES.<sup>18</sup> The pseudo-pH values of N<sub>2</sub>-saturated DMF/buffer solutions were found to be similar to those of  $CO_2$ -saturated DMF/H<sub>2</sub>O solutions.<sup>19</sup> Addition of the buffer solution under N<sub>2</sub> resulted in a continuous increase of current in the CV measurements (Fig. 3a). The CPE experiment with a 9.0% v/v buffer solution under an N<sub>2</sub> atmosphere, where the pseudo-pH value of the bulk solution is similar to that of a  $CO_2$ -saturated DMF solution solution with FE of 84% (Table 1, entry 3). These findings indicate that



Fig. 3 (a) CVs of **Co(n)BIPC** (0.5 mM) in DMF with 0.1 M TBAPF<sub>6</sub> under an N<sub>2</sub> atmosphere at a scan rate of 100 mV s<sup>-1</sup> upon addition of buffer solution ranging from 0% v/v (black) to 14.4% v/v (purple). (b) Reaction rate dependence upon addition of H<sub>2</sub>O under a CO<sub>2</sub> atmosphere (black) and upon addition of buffer solution under an N<sub>2</sub> atmosphere (blue) determined at -2.17 V in the CV results with a scan rate of 100 mV s<sup>-1</sup>.



Fig. 4 Catalytic Tafel plots of Co(II)TPP (black), Co(II)BIPC with 5 M  $H_2O$  (red) and Co(II)BIPC with 5 M TFE (blue).

**Co**(**n**)**BIPC** is able to function both as a CO<sub>2</sub> reduction catalyst and an H<sub>2</sub> evolution catalyst under the same pseudo-pH conditions. However, the apparent catalytic rate constants ( $k_{obs}$ ) of CO<sub>2</sub> reduction and H<sub>2</sub> evolution suggest that the reaction rates of CO<sub>2</sub> reduction are clearly faster than those of H<sub>2</sub> evolution in the range of pseudo-pH from 7.44 to 8.53 (Fig. 3b).<sup>20</sup> In particular, the rate constant under CO<sub>2</sub> in the presence of 5 M H<sub>2</sub>O is 2.6 times greater than the rate constant measured under N<sub>2</sub> in the presence of 9.0% v/v buffer solution (Table 1 and Fig. 3b). The difference in the reaction rates between CO<sub>2</sub> reduction and H<sub>2</sub> evolution supports the results of the selective CO<sub>2</sub> reduction by Co(**n**)BIPC.

The catalytic Tafel plots of Co(II)BIPC and Co(II)TPP clarify the electrochemical properties and give insights into the advantages of the monoanionic bipyricorrole ligand over the dianionic porphyrin ligand.<sup>21</sup> Each plot was obtained by determining the apparent catalytic rate constant values  $(k_{cat})$  of Co(II)BIPC with 5 M H<sub>2</sub>O, Co( $\pi$ )BIPC with 5 M TFE<sup>22</sup> and Co( $\pi$ )TPP<sup>23</sup> from the catalytic currents in the CV measurements, which gave  $k_{cat}$ of 7.8, 19.8 and 30.4 s<sup>-1</sup>, respectively (Fig. S22–S26, ESI†). Fig. 4 reveals that  $Co(\pi)BIPC$  is capable of working as a  $CO_2$  reduction catalyst with much smaller overpotential  $(\eta)$  than Co( $\pi$ )TPP formed by the dianionic ligand, whereas the reaction rate of  $Co(\pi)BIPC$  is similar to that of  $Co(\pi)TPP$ . In particular, the maximum TOF (TOF<sub>max</sub>) is achieved with  $\eta$  of 0.68 V by Co( $\pi$ )BIPC with 5 M H<sub>2</sub>O, which is 0.35 V more positive than Co(II)TPP in which the  $\eta$  for TOF<sub>max</sub> is 1.03 V. This result unambiguously demonstrates the advantage of the monoanionic ligand as a component of a CO<sub>2</sub> reduction catalyst to decrease the overpotential in the electrochemical reaction.

In summary, **Co**(**u**)**BIPC**, which consists of the Co(**u**) complex with a monoanionic bipyricorrole ligand possessing a 2,6-dimethoxyphenyl group at the *meso*-position, catalyzes a selective CO<sub>2</sub> reduction reaction in the presence of proton sources, as confirmed by CPE experiments.<sup>24</sup> Although Co(**u**)**BIPC** was found to function both as a CO<sub>2</sub> reduction catalyst and an H<sub>2</sub> evolution catalyst under the same pseudo-pH conditions, the difference in reaction rates between CO<sub>2</sub> reduction and H<sub>2</sub> evolution leads to a selective CO<sub>2</sub>-to-CO reduction under a CO<sub>2</sub> atmosphere. Furthermore, we have demonstrated using catalytic Tafel plots that the monoanionic ligand is useful for generating an electrocatalytically active low-valent species at much more positive potentials than a dianionic porphyrinoid ligand. Compared to our previous work using a Co(**u**) complex of tetradehydrocorrin  $(E_{1/2}(\text{Co}^{II/I}) = -0.53 \text{ V})$  that promotes the selective H<sub>2</sub> evolution rather than CO<sub>2</sub> reduction, **Co(II)BIPC** exhibits a negatively shifted  $E_{1/2}(\text{Co}^{II/I})$  at -0.87 V and catalyzes selective CO<sub>2</sub>-to-CO reduction, indicating that the moderate stabilization of the Co(I) species is favorable to promote the selective CO<sub>2</sub> reduction reaction. We believe that the present findings will contribute to the development of efficient CO<sub>2</sub> reduction catalysts with low overpotential.

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#### Conflicts of interest

There are no conflicts to declare.

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- 20 Each  $k_{\rm obs}$  value was determined using the catalytic current at -2.17 V in the CV results depicted in Fig. S16, ESI† and Fig. 3a with a scan rate of 100 mV s<sup>-1</sup>, which are attributed to CO<sub>2</sub> reduction and H<sub>2</sub> evolution, respectively.
- 21 **Co(n)TPP** was confirmed to catalyze selective CO<sub>2</sub>-to-CO reduction with FE of 87%, whereas no  $H_2$  evolution was observed in the CPE experiment in the absence of  $H_2O$ .
- 22 The  $k_{\text{cat}}$  of Co(n)BIPC in the presence of 5 M TFE was determined using the  $i_{\text{cat}}$  at -2.28 V.
- 23 According to ref. 7*b*, Co(n)TPP does not show current dependence on the concentration of proton sources. Thus, the reaction rate in the absence of a proton source was calculated for Co(n)TPP.
- 24 Demethylated **Co(II)BIPC**, which was prepared according to ref. 6*a*, demonstrated no enhancement of the catalytic activity (Fig. S27, ESI†).