

Electronic Supplementary Information (ESI) for

**Highly selective CO<sub>2</sub> electrolysis in aqueous media by water-soluble cobalt dimethyl-bipyridine complex**

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## Experimental section

### Synthesis of Co complexes

Co complexes with bpy (2,2'-bipyridine)- and tpy (2,2':6',2''-terpyridine)-based ligands were synthesized according to a previously reported method.<sup>[1]</sup>

#### • [Co(4,4'-dimethyl-2,2'-bipyridine)<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub> ([Co-dmbpy])

Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Fujifilm Wako Pure Chemical, 1.5 mmol) and 4,4'-dimethyl-2,2'-bipyridine (dmbpy; Tokyo Chemical Industry, 4.5 mmol) were dissolved in methanol and stirred at room temperature for 2 h. The solution color changed to brown, and the solution was evaporated to dryness. The residue was recrystallized from methanol (Fujifilm Wako Pure Chemical) and diethyl ether (Fujifilm Wako Pure Chemical). Yield: 98%; *m/z* (ESI-MS): 305.6 [M]<sup>2+</sup>.

#### • [Co(2,2' :6' ,2'' -terpyridine)<sub>2</sub>](NO<sub>3</sub>)<sub>2</sub> ([Co-tpy])

Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (1.5 mmol) and 2,2' :6' ,2'' -terpyridine (tpy; Tokyo Chemical Industry, 3.0 mmol) were dissolved in methanol and stirred at room temperature for 2 h. The solution color changed to dark-brown, and the solution was evaporated to dryness. The residue was recrystallized from methanol and diethyl ether. Yield: 86%; *m/z* (ESI-MS): 262.6 [M]<sup>2+</sup>.

#### • [Co(2,2' -bipyridine)<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub> ([Co-bpy])

Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (2.5 mmol) and 2,2' -bipyridine (bpy; Kanto Chemical Co., 7.5 mmol) were dissolved in methanol and stirred at room temperature for 2 h. The solution color changed to brown, and the solution was evaporated to dryness. The residue was recrystallized from methanol and diethyl ether. Yield: 96%; *m/z* (ESI-MS): 263.1 [M]<sup>2+</sup>.

#### • [Co(4,4' -dimethoxy-2,2' -bipyridine)<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub> ([Co-dmobpy])

Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (1.5 mmol) and 4,4'-dimethoxy-2,2'-bipyridine (dmobpy; Tokyo Chemical Industry, 4.5 mmol) were dissolved in methanol and stirred at room temperature for 2 h. The solution color changed to brown, and the solution was evaporated to dryness. The residue was recrystallized from methanol and diethyl ether. Yield: 77%; *m/z* (ESI-MS): 353.6 [M]<sup>2+</sup>.

**·pseudo-two coordinate complex [Co(4,4'-dimethyl-2,2'-bipyridine)<sub>2</sub>]<sup>2+</sup> ([Co/dmbpy]=2/1)**

Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (Fujifilm Wako Pure Chemical, 1.5 mmol) and 4,4'-dimethyl-2,2'-bipyridine (dmbpy; Tokyo Chemical Industry, 3.0 mmol) were dissolved in methanol and stirred at room temperature for 2 h. The solution color changed to brown, and the solution was evaporated to dryness. The residue was recrystallized from methanol (Fujifilm Wako Pure Chemical) and diethyl ether (Fujifilm Wako Pure Chemical). Yield: 70%.

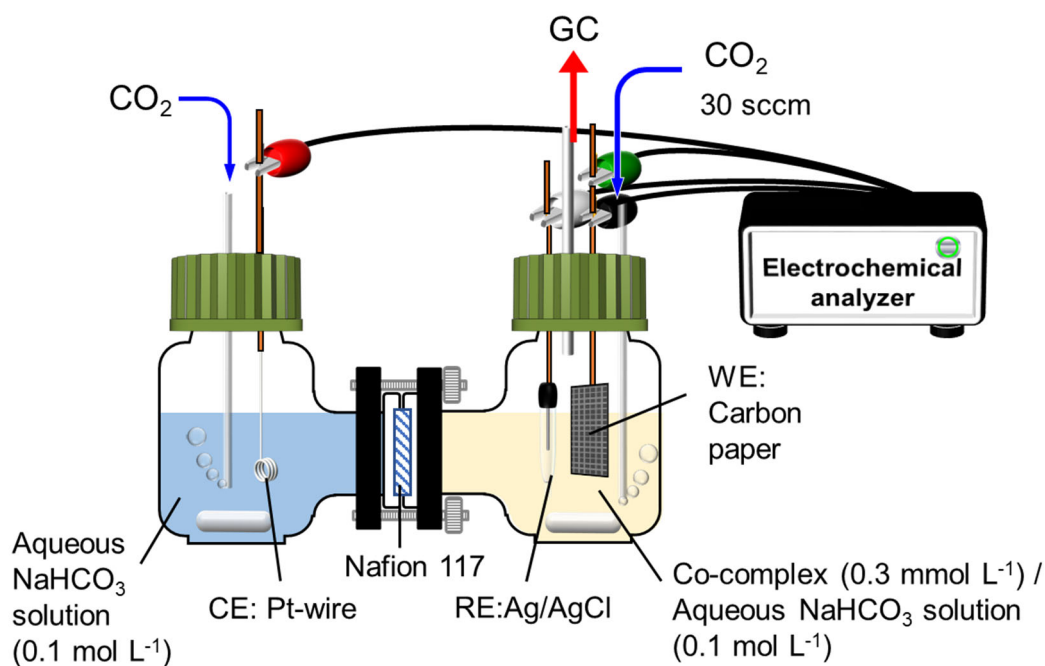
**Co complexes (commercial)**

[Co(II)(bpy)<sub>3</sub>]Cl<sub>2</sub> and [Co(III)(bpy)<sub>3</sub>]Cl<sub>3</sub> salts were purchased from Dyenamo Chemicals (purity > 95%). These complexes were used as received.

**Bulk electrolysis of CO<sub>2</sub> reduction**

Bulk electrolysis for CO<sub>2</sub> reduction was conducted in a H-shaped Pyrex sealed glass cell using an electrochemical analyzer (ALS612E, BAS) in a three-electrode system. The detailed configuration is shown in Fig. S1. A Nafion 117 membrane (Merck) served as the separator, aqueous 0.1 M NaHCO<sub>3</sub> solution (120 mL) was used as the electrolyte, and 0.3 mmol L<sup>-1</sup> Co complex catalyst was dissolved in this electrolyte for the cathode side. A carbon paper (CP) electrode (TGP-H-060, TORAY, 1.8 × 2.5 cm<sup>2</sup>), Pt wire, and a Ag/AgCl electrode (RE-1S, BAS) were used as the working, counter, and reference electrodes, respectively. All potentials were converted to the normal hydrogen electrode (NHE) reference scale using the relation  $E$  (V vs. NHE) =  $E$  (V vs. Ag/AgCl) + 0.199 V.

Before the electrochemical tests, both parts of the electrolyte were purged with CO<sub>2</sub> gas for pre-saturation. The flow rate was then maintained at 30 sccm during the catalytic process. The amounts of CO, H<sub>2</sub>, and CH<sub>4</sub> in the gas phase were determined by gas chromatography; the gas chromatograph (Inficon, Micro GC Fusion 3-module system; module A: Rt-Molsieve 5A column, thermocouple detector (TCD), Ar carrier for H<sub>2</sub>; module B: Rt-Molsieve 5A column, TCD, He carrier for CO and CH<sub>4</sub>) was directly connected to the reaction cell. The amount of HCOO<sup>-</sup> in the solution was analyzed after electrolysis by ion chromatography (ICS-211, Dionex) with IonPacAS15 and IonPacAG15 columns. UV-Vis-NIR spectra of the electrolyte were obtained using a UV-Vis-NIR spectrophotometer (JASCO, V-780).



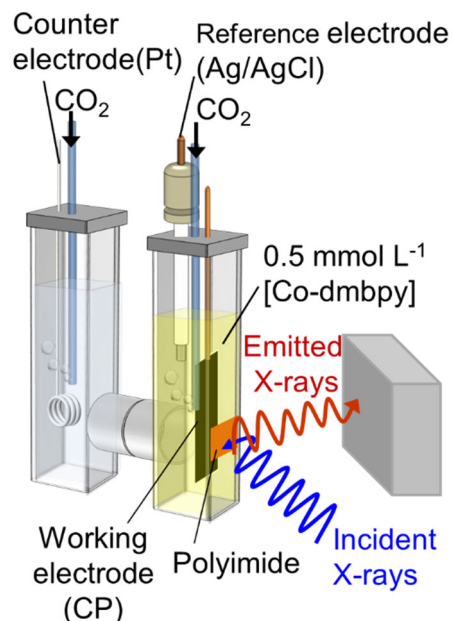
**Fig. S1** Schematic of the experimental setup for bulk electrolysis of CO<sub>2</sub> reduction.

### Operando X-ray absorption spectroscopy (XAS)

Co *K*-edge X-ray absorption near edge structure (XANES) analyses were conducted via fluorescence yield detection with a four-element silicon drift detector (SDD) using the BL33XU beamline at SPring-8 (Hyogo, Japan). The incident X-rays were monochromatized using a channel-cut Si single crystal

and slightly tilted Rh mirrors. When acquiring operando XAS data, we used two types of cells with two compartments. The detailed configurations are shown in Figs. S2 and S11a.

In the case of the measurement shown in Fig. 3a, the working electrode compartment of the cell facing the X-ray beam had a 7 mm × 5 mm square window hole, and the hole was covered with a 100 μm-thick polyimide film; the edges were sealed with silicone rubber. The CP used as the working electrode was placed in the center of the cathode cell containing the aqueous [Co-dmbpy] solution and was positioned ~5 mm from the polyimide film. In the case of the measurement shown in Fig. S5a, the working-electrode compartment had a round window hole 1 cm in diameter; the window was directly covered with CP and then sealed with 100 μm-thick polyimide. Because the CP is porous, the aqueous solution soaked through to the interface with the polyimide film, forming a very thin layer of aqueous solution. The incident X-rays entered at an angle of 45° with respect to the window normal, and the fluorescence signal was detected orthogonally (Fig. S4a).



**Fig. S2** Schematic image of *operando*-XAS apparatus for CO<sub>2</sub> reduction in an aqueous solution at cathode compartment (cell on the right).

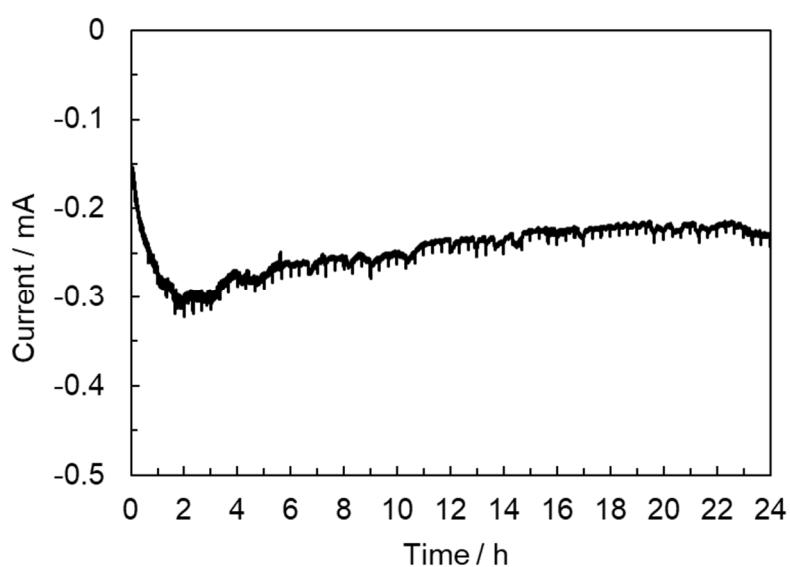
A calculation to estimate the transmission decay of incident and fluorescent X-rays confirmed that the X-ray absorption near edge structure (XANES) originated from [Co-dmbpy] and not from CP, because the system can detect fluorescence within a depth of  $\sim 0.2$  mm from the polyimide window (Fig. S10).

### Density functional theory (DFT) calculations

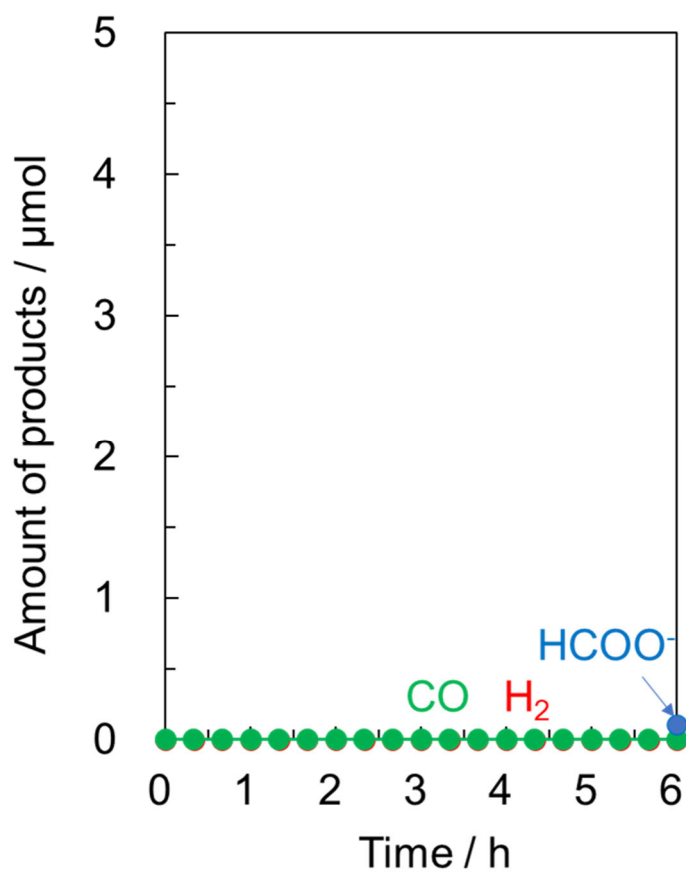
DFT calculations were performed using the B3LYP functional<sup>[2-4]</sup> in the Gaussian 09 package (Revision E.01). The 6-31G(d,p) basis set<sup>[5]</sup> was used for H, C, N, and O, while the Lanl2DZ basis set<sup>[6]</sup> was employed for Co. The solvation effect was accounted for using the conductor-like polarizable continuum model (CPCM)<sup>[7]</sup> for water. After geometry optimization, vibrational analyses were performed on the optimized geometries, and the absence of an imaginary number frequency was confirmed for all the optimized structures. The Gibbs free energy ( $G$ ) of each species was determined by structural optimization and vibrational calculations. The free energy of H<sup>+</sup>(aq) ( $G[\text{H}^+(\text{aq})]$ ) was set to  $-265.9$  kcal mol<sup>-1</sup><sup>[8]</sup>. The equilibrium potential was defined as the state at which the Gibbs free

energy of electrons ( $G[e^-]$ ) was equal to the Gibbs free energy difference of the reaction  $\text{CO}_2 + 2\text{H}^+ \rightarrow \text{CO} + \text{H}_2\text{O}$ . At each step of the reaction ( $1 \rightarrow 2, 3 \rightarrow 4$ ), electrons were supplied with an overpotential of 900 mV.

## Results

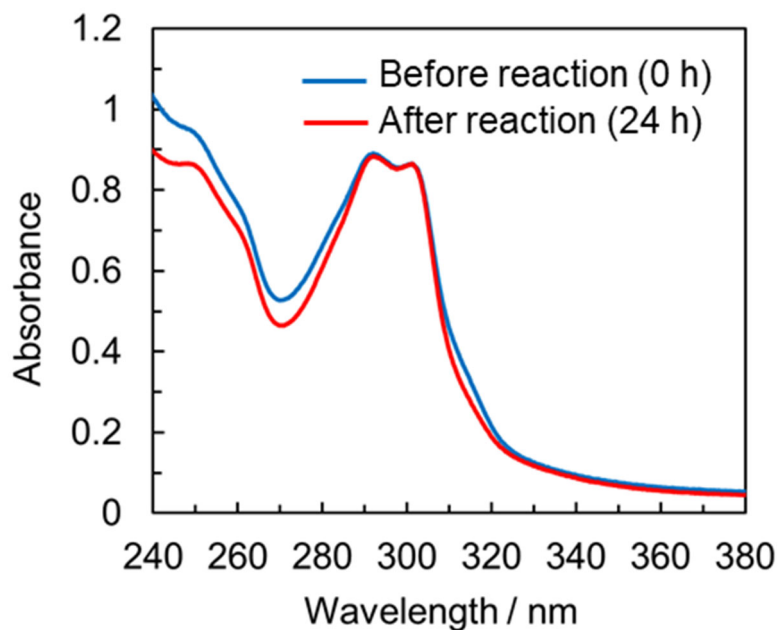


**Fig. S3** Time courses of the current during  $\text{CO}_2$  electrolysis of  $[\text{Co-dmbpy}]$  ( $0.3 \text{ mmol L}^{-1}$ ) at in aqueous  $\text{NaHCO}_3$  ( $0.1 \text{ mol L}^{-1}$ ,  $\text{CO}_2$  bubbling, pH 6.8) at  $-0.85 \text{ V}$  vs. NHE. The spikes in the traces are due to the sampling of the headspace for GC analysis.



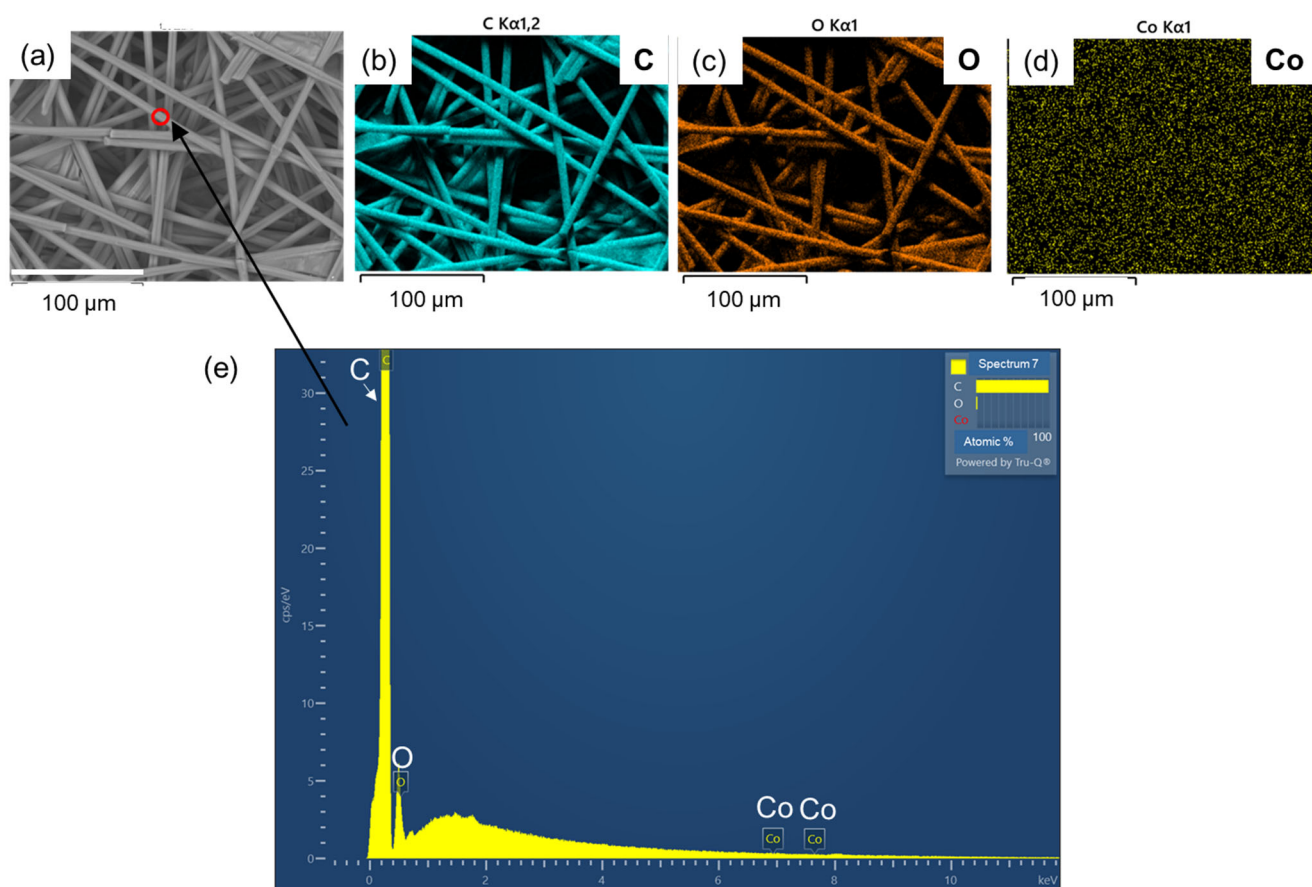
**Fig. S4** Electrolysis of [Co-dmbpy] ( $0.3 \text{ mmol L}^{-1}$ ) in aqueous  $\text{NaHCO}_3$  ( $0.1 \text{ mol L}^{-1}$ ) under Ar bubbling (adjusted to pH 6.8) at  $-0.85\text{V}$  (vs. NHE).





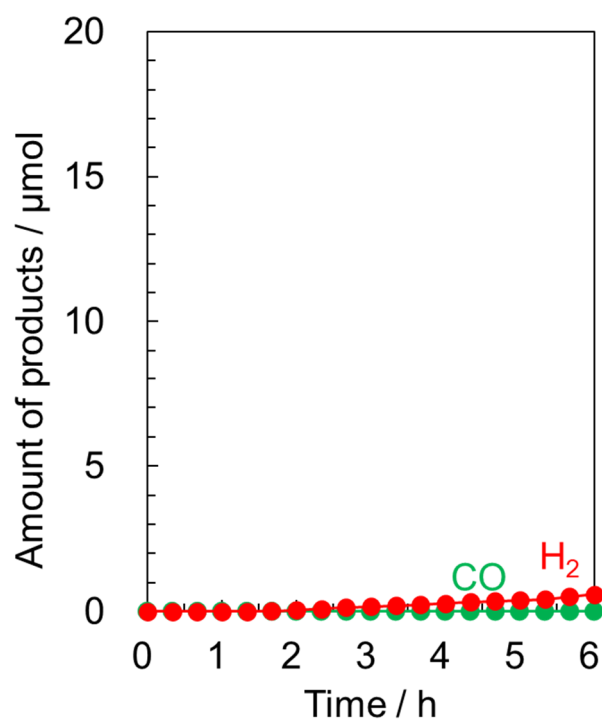
**Fig. S5** UV-vis absorption spectra of the electrolyte solution before (0 h, blue line) and after (24 h, red line) CO<sub>2</sub> electrolysis. Both samples were diluted with an equal volume of pure water before being measured.

The peak heights of the Co complexes at 293 nm and 301 nm before and after the reaction differ only by 0.5% and 0.2%, respectively, confirming that the amount of water-soluble Co complexes is almost unchanged before and after the electrolysis reaction. Therefore, even if Co complexes adhered to the electrode as insoluble heterogeneous species, the possibility is estimated to be less than 0.5% of the total complexes, and the heterogeneous species should have little influence on the experimental results.



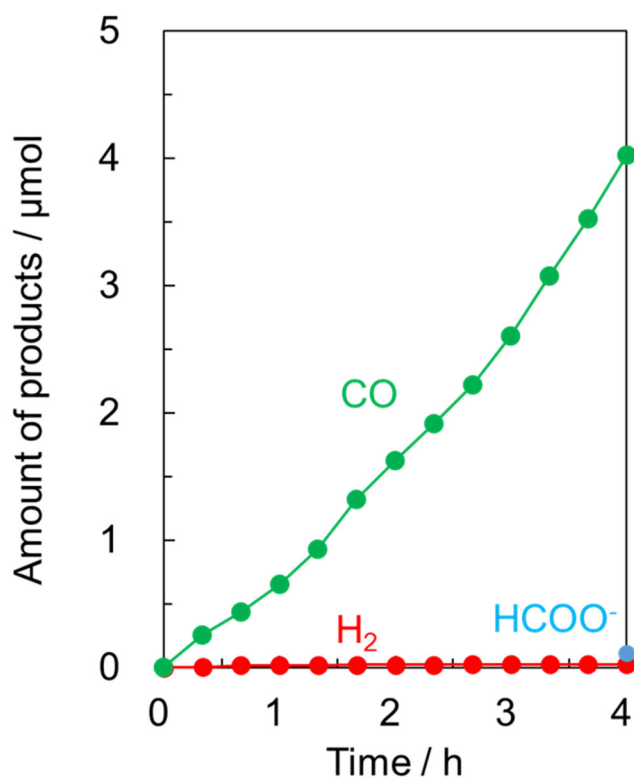
**Fig. S6** Results of scanning electron microscopy (SEM) for a CP electrode after CO<sub>2</sub> electrolysis with Co-dmbpy catalyst (0.3 mmol L<sup>-1</sup>) in an aqueous NaHCO<sub>3</sub> (0.1 mol L<sup>-1</sup>) at -0.85 V (vs. NHE) for 24 h (shown in Fig. 2). (a) SEM image, and (b)-(e) SEM/energy-dispersive X-ray spectrometry (SEM-EDS) data. SEM-EDS was performed using an SU3500 microscope (Hitachi High-Tech Corp.).

As shown in the SEM image in (a), no heterogeneous precipitates or adsorbed species were detected on the carbon fiber surface of the CP electrode. In the SEM-EDS mapping of Co in (d) and the spectrum in (e), the atomic concentration of Co in the catalytic species was measured to be 0.00 at.%, which was below the detection limit and no heterogeneous Co species were detected.

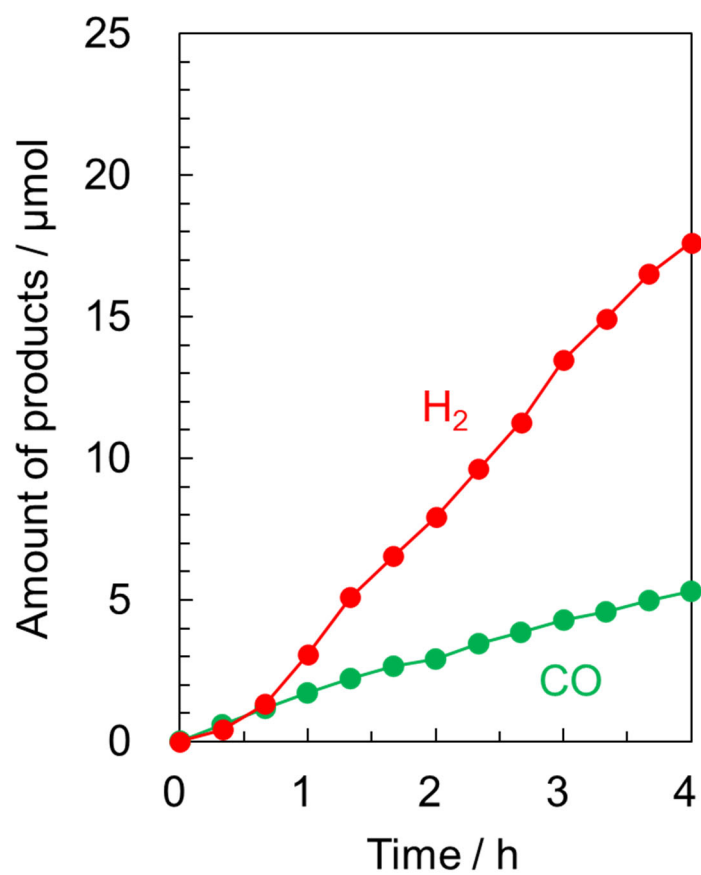


**Fig. S7** A dip test for CO<sub>2</sub> electrolysis in an aqueous NaHCO<sub>3</sub> (0.1 mol L<sup>-1</sup>) solution without Co-dmbpy at -0.85 V vs. NHE (pH 6.8) under CO<sub>2</sub> flow (1 atm). The CP electrode was reused after CO<sub>2</sub> electrolysis with Co-dmbpy in solution for 24 h (shown in Figs. 2 and S6).

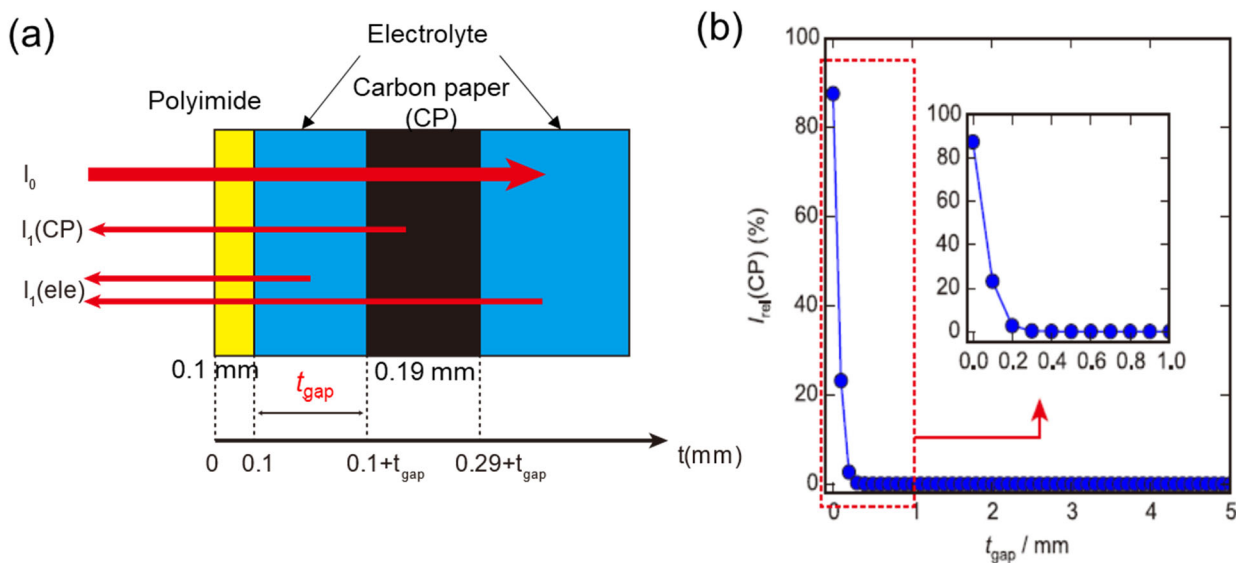
In the absence of the Co-dmbpy catalyst, CO production was below the detection limit, only a small amount of hydrogen was produced, and the CO<sub>2</sub> reduction reaction did not proceed. These experimental results indicate that homogeneous [Co-dmbpy] species in aqueous solution act as a catalyst for CO<sub>2</sub> reduction.



**Fig. S8** CO<sub>2</sub> electrolysis of 0.3 mmol L<sup>-1</sup> [Co-dmbpy] at -0.80 V vs. NHE in an aqueous 0.1 mol L<sup>-1</sup> NaHCO<sub>3</sub> solution bubbled with CO<sub>2</sub> (pH 6.8) (Table S1, entry 1).



**Fig. S9** CO<sub>2</sub> electrolysis of 0.3 mmol L<sup>-1</sup> [Co-dmbpy] at -1.30 V vs. NHE in an aqueous 0.1 mol L<sup>-1</sup> NaHCO<sub>3</sub> solution bubbled with CO<sub>2</sub> (pH 6.8). (Table S1, entry 4)

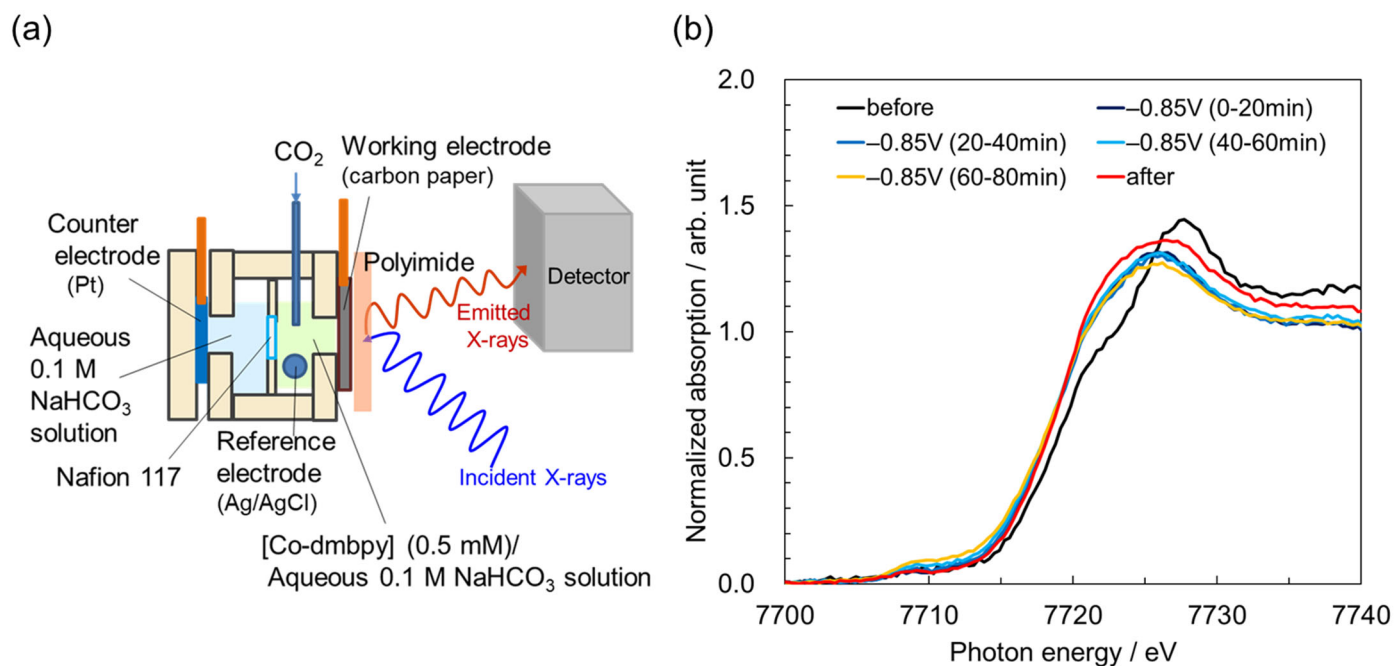


**Fig. S10** Model used to estimate decay of the incident X-rays and the Co *K*-edge X-ray fluorescence signal in XAS measurements. (a) Electrode arrangement in the model used for the calculations. (b) Relationship between the ratio of total  $I_1(\text{CP})$  to the total emitted X-ray intensity ( $I_{\text{rel}}(\text{CP})$ ) and the distance between the polyimide and CP ( $t_{\text{gap}}$ ).

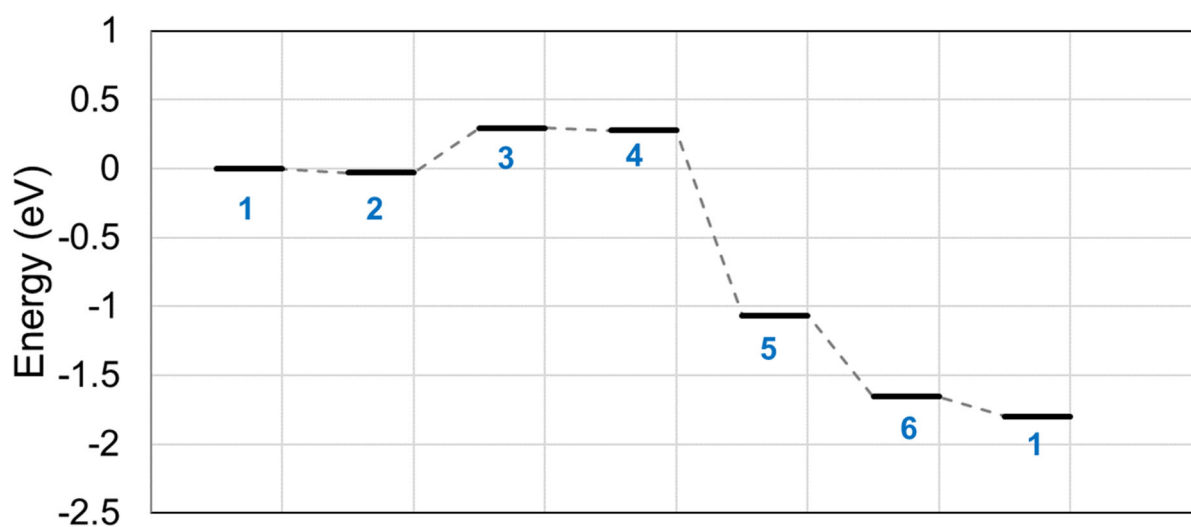
For the calculations, we assumed that the incident X-rays with an intensity of  $I_0$  entered vertically and then the emitted X-rays from the CP and electrolyte were attenuated to be detected as intensities  $I_1(\text{CP})$  and  $I_1(\text{ele})$ , respectively. We further assumed that both the incident and emitted X-ray energies were consistent at 7700 eV and that the influence of the electrolyte in the porous CP was excluded because of its hydrophobicity. The ratio of the total  $I_1(\text{CP})$  to the total emitted X-ray intensity,  $I_{\text{rel}}(\text{CP})$  was calculated as

$$I_{\text{rel}}(\text{CP}) = \int I_1(\text{CP}) dt / (\int I_1(\text{CP}) dt + \int I_1(\text{ele}) dt) \times 100$$

In the case of the cell in Fig. S2 ( $t_{\text{gap}} = 5$  mm), the  $I_{\text{rel}}(\text{CP})$  value was calculated to be 0%, indicating that the Co *K*-edge X-ray fluorescence signal provides information about [Co-dmbpy] only in the bulk electrolyte. However, in the case of the cell shown in Fig. S11(a),  $t_{\text{gap}} = 0$  mm is assumed. The  $I_{\text{rel}}(\text{CP})$  value was determined to be ~90%, which demonstrates that the XAS signal includes information about Co on and in the vicinity of the surface of the CP.



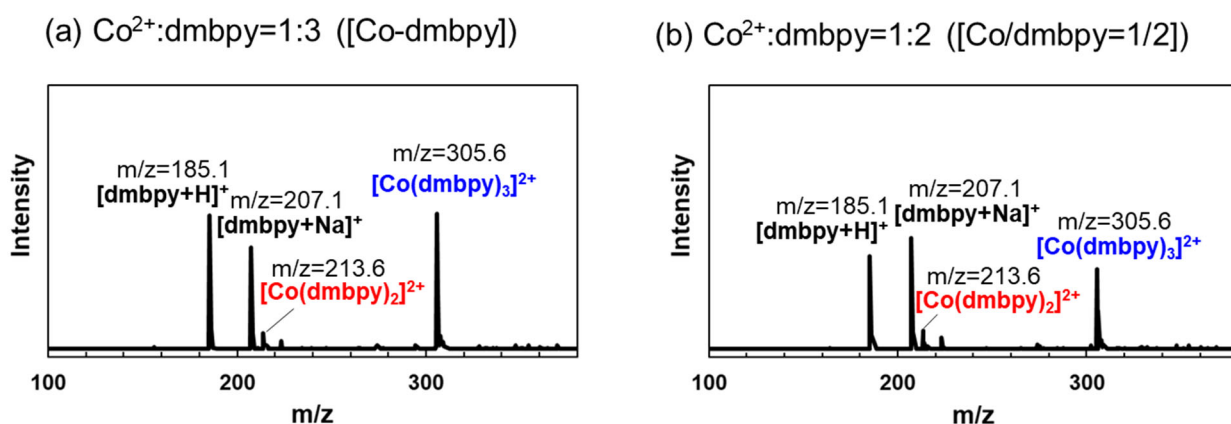
**Fig. S11** (a) Schematic of the experimental operando XAS apparatus used to acquire data during the bulk electrolysis of  $\text{CO}_2$  at a cathode supported on carbon paper (CP). The results in Fig. 3a in the main text are mainly intended to show the state of the Co components in an aqueous solution, whereas this measurement is mainly intended to detect Co components in the vicinity of the CP. See Fig. S3 for details. (b) *Operando* Co  $K$ -edge XANES spectra of [Co-dmbpy] recorded at the open-circuit voltage (before electrolysis: black; after electrolysis: red) and after  $\text{CO}_2$  electrolysis ( $-0.85$  V vs. NHE, pH 6.8) of  $0.3 \text{ mmol L}^{-1}$  [Co-dmbpy] in a aqueous  $0.1 \text{ mol L}^{-1}$   $\text{NaHCO}_3$  solution. Similar to the measurement in solution in Fig. 3a, a shift of the peak to the lower-energy side upon application of a potential was observed in the measurement performed near the CP.



**Fig. S12** Energy diagram based on DFT calculations for two-coordinated complex; electrons are supplied at each step, which takes into account of electron transfer process (**1** to **2** and **3** to **4** of **Fig. 3b**; overpotential 900 mV).<sup>[9]</sup> The numbers (**1-6**) correspond to the structures in the reaction mechanism in **Fig. 3b**.

The results show that steps **2** to **3** of the CO<sub>2</sub> configuration have the highest energy barrier and are the rate-limiting steps in the CO<sub>2</sub> reduction reaction.

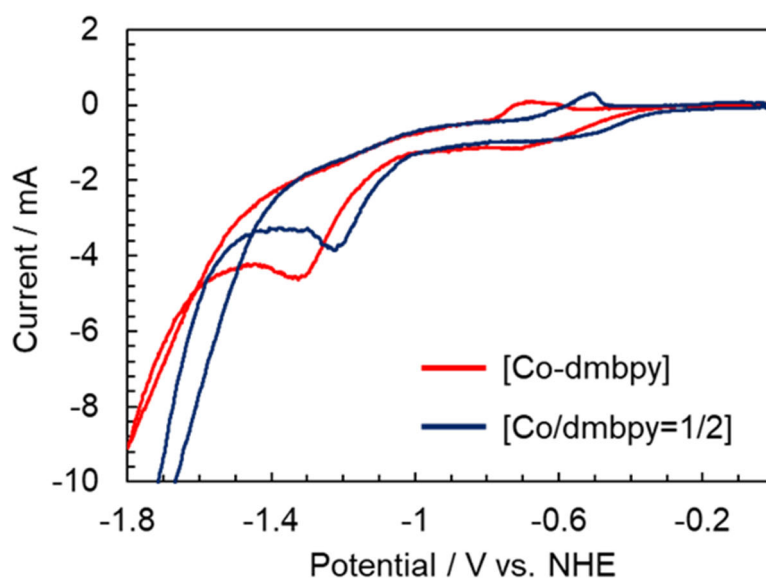




**Fig. S13** ESI-MS spectrum of  $[\text{Co-dmbpy}]$  and  $[\text{Co/dmbpy}=1/2]$  dissolved in methanol.

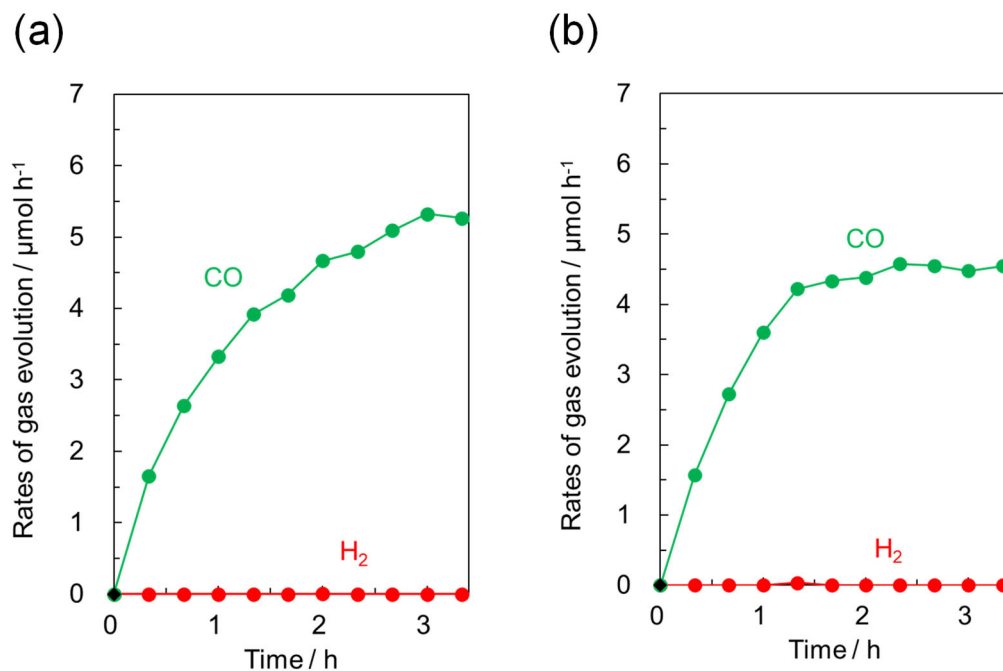
When synthesized with a  $\text{Co/dmbpy}$  ratio of  $1/2$  (hereafter,  $[\text{Co/dmbpy}=1/2]$ ), the spectrum is similar to that of the three-coordinated  $[\text{Co-dmbpy}]$ , and molecular ions of the three-coordinate were also detected.

On the other hand, a crystal analysis of the two-coordinate  $[\text{Co}(\text{bpy})_2(\text{NO}_3)](\text{NO}_3)$  with an unsubstituted bpy (2,2'-bipyridine) ligand using a similar synthetic method was reported.<sup>[10]</sup> Therefore, we assumed that some of the  $[\text{Co/dmbpy}=1/2]$  complexes synthesized at a ratio of  $1/2$  were likely to form a two-coordination system. However, the structure was unclear, and we regarded  $[\text{Co/dmbpy}=1/2]$  as a two-coordination system and performed  $\text{CO}_2$  electrolysis.



**Fig. S14** Current voltage curves for [Co-dmbpy] (red) and [Co/dmbpy=1/2] (dark blue, synthesized  $\text{Co}^{2+}$  with 2 equiv. of dmbpy) ( $0.3 \text{ mmol L}^{-1}$ ) in aqueous  $\text{NaHCO}_3$  ( $0.1 \text{ mol L}^{-1}$ ,  $\text{CO}_2$  bubbling, pH 6.8).

The potentials at which the two reduction waves begin to flow in the CV curves for [Co/dmbpy=1/2] were both slightly more positive than those for [Co-dmbpy]. It was confirmed that the CV curves of [Co-dmbpy] and [Co/dmbpy=1/2] showed almost the same shape of the CV curves and current values around  $-0.85 \text{ V vs. NHE}$  where electrolysis was performed.



**Fig. S15** CO<sub>2</sub> electrolysis of (a) [Co-dmbpy] (0.3 mmol L<sup>-1</sup>) and (b) [Co/dmbpy(1/2)] (synthesized with a Co/dmbpy ratio of 1/2) (0.3 mmol L<sup>-1</sup>) in an aqueous NaHCO<sub>3</sub> (0.1 mol L<sup>-1</sup>, 120 mL) solution at -0.85 V vs. NHE (pH 6.8) under CO<sub>2</sub> flow (1 atm).

The CO<sub>2</sub>RR for [Co-dmbpy] in **Fig. 2b** is plotted hourly, but to clarify the induction period, measurements are shown every 20 minutes for comparison. The induction period for CO formation in the case of [Co-dmbpy] was 3 h, whereas the induction period was 1 h 20 min. in the case of the similar two-coordinate [Co/dmbpy (1/2)], reducing the induction period by more than half. Since the structure of [Co/dmbpy (1/2)] is difficult to determine by ESI-MS, this is only a speculation, but it suggests that the two-coordinated Co complex forms the active species more rapidly (shorter induction period) than the three-coordinated one.



**Table S1** Rate of products and CO selectivity for CO<sub>2</sub> electrolysis of 0.3 mmol L<sup>-1</sup> Co compound in an aqueous NaHCO<sub>3</sub> (0.1 mol L<sup>-1</sup>) solution at various potentials for 3 h.<sup>a</sup>

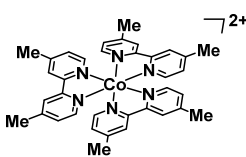
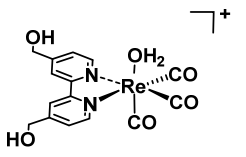
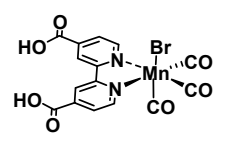
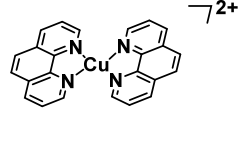
Entry	Potential / V vs. NHE (pH 6.8)	Difference from theoretical equilibrium potential <sup>b</sup> / mV	Rate of products, 3 h / μmol h <sup>-1</sup>		CO selectivity <sup>c</sup> / %
			CO	H <sub>2</sub>	
1	-0.80	270	0.88	0.00	99.2
2	-0.85	320	5.02	0.00	100.0
3	-0.95	420	4.02	0.20	94.9
4	-1.30	770	1.33	6.62	28.7

<sup>a</sup> Carbon paper, Ag/AgCl, and platinum wire were used as working, reference, and counter electrodes, respectively. The pH of the 0.3 mmol L<sup>-1</sup> Co compound/ NaHCO<sub>3</sub> (0.1 mol L<sup>-1</sup>) aqueous solution saturated with CO<sub>2</sub> was approximately 6.8. Electrolysis was performed for 3 hours, and the product rate at 3 hours is shown.

<sup>b</sup> references [11, 12]

<sup>c</sup> Calculated from the amount of CO generated in relation to the total amount of reduced products (CO, H<sub>2</sub>, and HCOO<sup>-</sup>) for 3 h.

**Table S2** Water-soluble molecular catalyst with polypyridine ligands for electrochemical CO<sub>2</sub> reduction in an aqueous solution.

Water-soluble molecular catalyst	Electrolyte	Working electrode	Applied potential / V	Products (FE%)	Maximum test time / h	Ref.
	0.1 M NaHCO <sub>3</sub> (pH 6.8, under CO <sub>2</sub> )	Carbon paper	-0.85 vs NHE (-0.45 vs RHE)	CO (99 ± 1%)	24	This work
			-0.80 vs NHE (-0.40 vs RHE)	CO (99 ± 1%)	4	This work
	0.1 M Na <sub>2</sub> SO <sub>4</sub> + 0.1 M NaOH (pH 6.9, under CO <sub>2</sub> )	Glassy carbon	-1.1 vs NHE	CO (95% <sup>a</sup> ) HCOO <sup>-</sup> (4% <sup>a</sup> )	3	[13]
	0.1 M KCl + 0.5 M K <sub>2</sub> CO <sub>3</sub> (pH 9, under CO <sub>2</sub> )	Hg pool	-1.4 vs Ag/AgCl	CO (65 ± 15%)	22	[14]
	0.1 M KHCO <sub>3</sub>	Graphene-modified carbon paper	-0.6 vs RHE	CO (~60%) HCOO <sup>-</sup> (~30%)	2	[15]

<sup>a</sup> Selectivity of product

**Table S3.** Cartesian coordinates (in Å) and energies (in hartree) for molecular species discussed in the text. Geometries optimized used DFT-B3LYP and 6-31G (d,p) basis sets for all atoms except Co, for which the LANL2DZ basis sets were used. The solvation effect was considered using the CPCM solvation model for water.

e<sup>-</sup>

Total Energy = -0.110813 (referenced to the potential of CBM of CGZS (-1.3 V vs RHE))

**CO<sub>2</sub>**

C	0.00000000	0.00000000	0.00000000
O	0.00000000	-0.00000000	1.16897207
O	0.00000000	0.00000000	-1.16897207

Total Energy (gas phase) = -188.590066

**CO**

C	0.00000000	0.00000000	-0.65029691
O	0.00000000	0.00000000	0.48772269

Total Energy (gas phase) = -113.323563

**H<sub>2</sub>O**

O	0.00000000	0.00000000	0.12018399
H	-0.00000000	0.75668951	-0.48073595
H	-0.00000000	-0.75668951	-0.48073595

Total Energy = -76.423071

**bpyMe<sub>2</sub>**

C	-1.48276023	0.72953014	-0.25776829
C	-3.47585960	-0.47107961	0.26315985
C	-2.66642151	-1.57310927	0.54224578
N	-1.33344265	-1.56940633	0.44336830
C	-0.74603268	-0.42064189	0.05063070
C	1.48275663	0.72954076	0.25773515
C	0.74603288	-0.42064110	-0.05063600
N	1.33344619	-1.56941173	-0.44335086
C	2.66642469	-1.57311116	-0.54223338
C	3.47585923	-0.47107263	-0.26317215
H	-0.97384593	1.62501555	-0.60022281
H	-4.55397220	-0.54789371	0.36536174
H	-3.12002361	-2.50861543	0.86600170
H	0.97383917	1.62503616	0.60015885
H	3.12002881	-2.50861925	-0.86598087
H	4.55397112	-0.54788105	-0.36538572
C	3.69048789	1.94729319	0.48808718
H	3.40526525	2.79091729	-0.14956310
H	4.75980815	1.76639822	0.35716416
H	3.52004136	2.25697788	1.52476158
C	-3.69048868	1.94729757	-0.48806304
H	-3.40590931	2.79062121	0.15027860
H	-4.75986819	1.76612638	-0.35800946
H	-3.51933076	2.25760074	-1.52443100
C	2.87905954	0.72183935	0.15348755
C	-2.87906294	0.72182839	-0.15351599

Total Energy = -573.868964

**[Co(bpyMe<sub>2</sub>)<sub>3</sub>]<sup>2+</sup>**

Co	-0.00019575	0.00019932	0.00014519
C	1.64497638	3.82036509	2.40757653
C	0.85727572	3.90618309	1.25514667
C	0.42245132	2.74969428	0.60743575
N	0.74637255	1.51483713	1.06937670

C	1.49613869	1.42312370	2.18058347
C	1.95820229	2.53643267	2.87023361
C	-0.84794756	3.90832344	-1.25478397
C	-1.63601733	3.82449532	-2.40710221
C	-1.95272318	2.54134857	-2.86959189
N	-0.74328382	1.51671064	-1.06885484
C	-0.41608863	2.75074059	-0.60702992
C	2.39235673	-3.52615509	2.26474599
C	2.94998151	-2.80405185	1.20664476
C	2.24372206	-1.76271943	0.59754905
N	0.99219647	-1.43552323	1.00827901
C	0.44707265	-2.12515185	2.02686147
C	1.10451885	-3.15919465	2.67661086
C	4.13918555	-1.04738246	-0.92899983
C	4.59719216	-0.27583018	-2.00187236
C	3.66992099	0.56814657	-2.62753509
C	2.36095482	0.60721340	-2.16114497
N	1.92945971	-0.13778081	-1.13435887
C	2.80291175	-0.96459287	-0.52403551
C	-1.49348479	1.42688412	-2.17992273
C	-2.24762960	-1.75813053	-0.59783579
N	-0.99539177	-1.43341666	-1.00835655
C	-0.45148295	-2.12404361	-2.02687871
C	-1.11089458	-3.15669904	-2.67685906
C	-4.14170613	-1.03943715	0.92884681
C	-4.59826501	-0.26714142	2.00178068
C	-3.66941323	0.57508323	2.62748661
C	-2.36040786	0.61180304	2.16105552
N	-1.93028393	-0.13393727	1.13421875
C	-2.80527953	-0.95907155	0.52385250
C	-2.39957931	-3.52101860	-2.26531965
C	-2.95590770	-2.79793314	-1.20719091
C	2.14910567	5.05273927	3.10700660
C	-2.13695173	5.05812481	-3.10661634
C	3.13739294	-4.64732605	2.93603158
C	6.02466049	-0.35428785	-2.47318322
C	-6.02590268	-0.34278997	2.47303947
C	-3.14693712	-4.64031272	-2.93715274
H	0.58331989	4.88065430	0.86953012
H	1.72616321	0.42368031	2.52566686
H	2.55697022	2.39571629	3.76360885
H	-0.57138767	4.88209041	-0.86924884
H	-2.55201619	2.40213050	-3.76285072
H	3.93806913	-3.06658149	0.84968507
H	-0.54941446	-1.82341581	2.32403665
H	0.60969705	-3.67470456	3.49271503
H	4.83386364	-1.69814892	-0.41161955
H	3.96160622	1.19296987	-3.46538276
H	1.62469331	1.25604396	-2.62552527
H	-1.72622945	0.42802669	-2.52489248
H	0.54568520	-1.82429172	-2.32375588
H	-0.61694242	-3.67318547	-3.49287122
H	-4.83757822	-1.68889818	0.41142675
H	-3.95992297	1.20033550	3.46542424
H	-1.62294804	1.25922610	2.62549121
H	-3.94457101	-3.05853424	-0.85040840
H	3.18919092	5.24825351	2.82069208
H	1.55869631	5.93289200	2.84308646
H	2.12901425	4.92501134	4.19257080
H	-3.17689379	5.25571981	-2.82122706
H	-1.54493388	5.93696529	-2.84193289
H	-2.11612624	4.93065157	-4.19220272
H	2.54517065	-5.56789739	2.92086182
H	4.09548160	-4.84225637	2.45012336
H	3.32716243	-4.40409524	3.98708505
H	6.45333052	0.64571594	-2.58947694
H	6.64642254	-0.92232043	-1.77790733
H	6.07558110	-0.84348665	-3.45246872
H	-6.45390166	0.65800695	2.58510974



H	-6.64789360	-0.91311915	1.77985752
H	-6.07745328	-0.82790556	3.45430289
H	-3.33982307	-4.39424646	-3.98699960
H	-2.55500208	-5.56110101	-2.92619157
H	-4.10368943	-4.83609917	-2.44896032

Total Energy = -1866.484551

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**[Co(bpyMe<sub>2</sub>)<sub>2</sub>]<sup>2+</sup>**

Co	0.0000002	0.0000918	0.0001479
C	3.7682245	-2.6660118	-1.1966813
C	3.8693621	-1.3759343	-0.6625213
C	2.7274855	-0.6888472	-0.2599249
N	1.4923488	-1.2472683	-0.3550795
C	1.3809445	-2.4685920	-0.9082371
C	2.4811420	-3.2022500	-1.3294174
C	3.8695618	1.3755886	0.6627092
C	3.7686101	2.6657145	1.1967889
C	2.4816037	3.2021447	1.3295089
C	1.3812988	2.4686065	0.9084010
N	1.4925281	1.2472262	0.3553368
C	2.7275840	0.6886322	0.2601762
C	-2.7275155	0.6887966	-0.2601942
N	-1.4924283	1.2473721	-0.3550893
C	-1.3810811	2.4687875	-0.9080518
C	-2.4812949	3.2023653	-1.3293303
C	-3.8695143	-1.3757439	0.6622943
C	-3.7685003	-2.6658175	1.1964860
C	-2.4814549	-3.2020954	1.3294346
C	-1.3811695	-2.4684814	0.9084090
N	-1.4924524	-1.2471630	0.3552131
C	-2.7275519	-0.6886968	0.2598703
C	-3.7683333	2.6659419	-1.1969057
C	-3.8694050	1.3757879	-0.6629165
C	4.9878051	-3.4396359	1.6115278
C	4.9883095	3.4392027	1.6115401
C	-4.9881696	-3.4393933	1.6111622
C	-4.9879398	3.4394652	-1.6118640
H	4.8409551	-0.9032880	-0.5839974
H	0.3792663	-2.8612993	-1.0257640
H	2.3263978	-4.1832293	-1.7646395
H	4.8410924	0.9028139	0.5841810
H	2.3270032	4.1831836	1.7646484
H	0.3796709	2.8614611	1.0258935
H	-0.3794300	2.8616450	-1.0253261
H	-2.3265966	4.1834301	-1.7643765
H	-4.8410802	-0.9030661	0.5836211
H	-2.3268093	-4.1830705	1.7647013
H	-0.3795192	-2.8612162	1.0260917
H	-4.8409549	0.9030171	-0.5846043
H	4.8047314	-3.9974719	-2.5336784
H	5.8480490	-2.7831154	-1.7574610
H	5.2482608	-4.1686112	-0.8351768
H	4.8053689	3.9970614	2.5337037
H	5.8484895	2.7825850	1.7574099
H	5.2487874	4.1681483	0.8351688
H	-4.8052911	-3.9971199	2.5334184
H	-5.8484436	-2.7828555	1.7568376
H	-5.2484588	-4.1684625	0.8348440
H	-5.2486058	4.1683276	-0.8354776
H	-4.8047859	3.9974210	-2.5339263
H	-5.8480820	2.7828575	-1.7580034

Total Energy = -1292.602126

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**[Co(bpyMe<sub>2</sub>)<sub>2</sub>]<sup>+</sup>**

Co	0.00000219	-0.00015918	0.00018014
C	-3.73929318	-2.63043235	1.28190584
C	-3.84628462	-1.35830280	0.71235044

C	-2.70763603	-0.67957237	0.27882132
N	-1.46152982	-1.22178863	0.37711778
C	-1.35337653	-2.43558577	0.95739878
C	-2.44694453	-3.15940953	1.41055902
C	-3.84596156	1.35867840	-0.71262623
C	-3.73866968	2.63076346	-1.28222113
C	-2.44620524	3.15948068	-1.41078632
C	-1.35281854	2.43547102	-0.95748644
N	-1.46126489	1.22172414	-0.37715730
C	-2.70747905	0.67974482	-0.27896860
C	2.70754123	0.67960335	0.27892880
N	1.46133119	1.22154196	0.37744773
C	1.35297594	2.43524168	0.95789277
C	2.44645048	3.15926570	1.41096314
C	3.84615831	-1.35849106	-0.71250536
C	3.73906330	-2.63062478	-1.28202878
C	2.44668082	-3.15954943	-1.41056414
C	1.35318353	-2.43566768	-0.95732255
N	1.46143906	-1.22186663	-0.37707816
C	2.70757446	-0.67969793	-0.27889568
C	3.73890291	2.63061906	1.28201259
C	3.84610191	1.35856669	0.71231868
C	-4.95158399	-3.39657323	1.73784307
C	-4.95077424	3.39713353	-1.73827269
C	4.95129575	-3.39684225	-1.73799784
C	4.95109728	3.39701401	1.73778064
H	-4.81957222	-0.88842970	0.62658828
H	-0.34961602	-2.82816771	1.06310506
H	-2.28634369	-4.13116935	1.86571792
H	-4.81934703	0.88899499	-0.62693797
H	-2.28537955	4.13118345	-1.86598667
H	-0.34897345	2.82785821	-1.06310246
H	0.34913613	2.82756571	1.06379568
H	2.28569715	4.13092610	1.86627944
H	4.81947793	-0.88867057	-0.62681802
H	2.28600337	-4.13131250	-1.86568745
H	0.34939715	-2.82820965	-1.06293908
H	4.81948989	0.88894212	0.62633837
H	-4.77816860	-3.86563692	2.71083198
H	-5.82896540	-2.75009540	1.81228383
H	-5.18447781	-4.19937963	1.02838624
H	-4.77707309	3.86643760	-2.71109219
H	-5.82819677	2.75075468	-1.81309663
H	-5.18377826	4.19976890	-1.02865661
H	4.77761940	-3.86641606	-2.71069048
H	5.82857259	-2.75029038	-1.81304229
H	5.18453538	-4.19925481	-1.02820620
H	5.18386577	4.19971248	1.02815927
H	4.77764495	3.86623882	2.71068369
H	5.82857196	2.75067242	1.81231625
Total Energy = -1292.724626			

**[Co(bpyMe<sub>2</sub>)<sub>2</sub>(CO<sub>2</sub>)<sup>+</sup>**

Co	0.03022783	-0.15317458	-0.90780510
C	2.64260611	-1.77065299	1.89502582
C	2.01288638	-1.07473321	0.86388474
N	0.69796996	-1.26318335	0.57682589
C	0.00370698	-2.14797111	1.31234027
C	0.57541206	-2.87224627	2.34977798
C	4.02018015	0.29355581	0.10634888
C	3.69608414	1.77504221	-1.74406141
C	2.37633727	1.35084343	-1.80745054
N	1.87830182	0.43901453	-0.95475357
C	2.68456451	-0.09275570	-0.00380153
C	-2.03799514	1.37970471	0.46306819
N	-0.70788479	1.46964230	0.23717661
C	-0.04911007	2.53812652	0.70610097
C	-4.04517594	-0.10912639	0.03556273
C	-3.72056476	-2.13711778	-1.18232011

C	-2.37564418	-1.81320863	-1.27904204
N	-1.85726995	-0.68788262	-0.75099902
C	-2.68241927	0.16774040	-0.09380178
C	-2.72931803	2.36891265	1.16634600
H	3.69313016	-1.60131957	2.09938264
H	-1.03927438	-2.27958600	1.05598894
H	-0.03713447	-3.57629162	2.90253628
H	4.64886171	-0.13924084	0.87529892
H	4.04953607	2.51649450	-2.45226909
H	1.68607149	1.72575922	-2.55341629
H	1.01516614	2.57757574	0.49971866
H	-4.68902715	0.58101842	0.56661474
H	-4.07739544	-3.05985485	-1.62670623
H	-1.67855060	-2.46681119	-1.78976883
H	-3.79626198	2.28288079	1.33271672
C	0.24552274	-0.98736096	-2.57043728
O	0.55649510	-2.01965792	-3.12673698
O	-0.17487615	0.17023121	-2.87540650
C	-6.06272738	-1.57854124	-0.39638365
H	-6.22001056	-2.60807293	-0.06114839
H	-6.54790058	-1.47944104	-1.37402469
H	-6.56141344	-0.90238029	0.30088230
C	5.99751984	1.66015052	-0.69086149
H	6.10345853	2.73699449	-0.84847203
H	6.57919380	1.15811416	-1.47278506
H	6.43723946	1.39955666	0.27421161
C	2.57605671	-3.43929590	3.79958586
H	2.21323094	-4.46945383	3.84915574
H	2.33256333	-2.96117376	4.75567138
H	3.66357969	-3.45208045	3.69967718
C	1.92754554	-2.69132329	2.66712219
C	4.55467971	1.24238384	-0.77156033
C	-0.67216617	3.55859007	1.41528388
C	-4.59486464	-1.27181276	-0.51136228
H	-0.08656824	4.40129024	1.76747518
C	-2.76305159	4.55616540	2.44286145
H	-3.84288449	4.51497345	2.28396660
H	-2.40366196	5.55106670	2.16572870
H	-2.57616897	4.42985463	3.51566742
C	-2.04884845	3.48628381	1.66177909

Total Energy = -1481.302791

**[Co(bpyMe<sub>2</sub>)<sub>2</sub>(CO<sub>2</sub>)<sup>0</sup>**

Co	-0.02740261	-0.06484439	-0.97935996
C	2.75724348	-1.77947487	1.86814334
C	2.08654537	-1.08042291	0.85475264
N	0.78079513	-1.30874063	0.58301646
C	0.13409009	-2.23477367	1.31022483
C	0.73596786	-2.96569894	2.32518279
C	4.08441718	0.31444906	0.13893462
C	3.81903382	1.80325978	-1.70936735
C	2.49907478	1.38579471	-1.79839383
N	1.95683538	0.48112648	-0.96215835
C	2.74235268	-0.06324069	-0.00189390
C	-2.12493636	1.35813396	0.49788038
N	-0.79542578	1.44445246	0.24788532
C	-0.12738331	2.50444715	0.73576089
C	-4.13616841	-0.15063190	0.15824769
C	-3.86697072	-2.10071962	-1.19112285
C	-2.54192328	-1.73321625	-1.38271480
N	-2.00124947	-0.62374892	-0.84269766
C	-2.79261083	0.16557415	-0.07344356
C	-2.79666990	2.33816446	1.23817731
H	3.80370038	-1.58276416	2.07064393
H	-0.91127765	-2.38862132	1.05955303
H	0.15752075	-3.70113992	2.87571358
H	4.69803558	-0.13030520	0.91361560
H	4.19857804	2.53893701	-2.41163569
H	1.83123441	1.75408394	-2.56978478

H	0.93405875	2.53919160	0.51241667
H	-4.74670540	0.48984780	0.78411107
H	-4.24218172	-3.00818149	-1.65374276
H	-1.86795079	-2.32927081	-1.98912354
H	-3.86244913	2.25393236	1.41609661
C	0.19290076	-0.89441094	-2.67765935
O	0.34845634	-2.05664278	-3.09527364
O	0.00919536	0.19775807	-3.30308590
C	-6.15003941	-1.65218192	-0.18221902
H	-6.25237070	-2.69246359	0.14268508
H	-6.71831725	-1.54890590	-1.11370375
H	-6.61185409	-1.00729859	0.56890125
C	6.08464448	1.69858920	-0.57314007
H	6.14415400	2.75535693	-0.28920719
H	6.61986779	1.59104257	-1.52234623
H	6.60845179	1.11319878	0.18607570
C	2.78359353	-3.51237160	3.71819305
H	2.76887803	-4.58683301	3.50492233
H	2.27756861	-3.36948370	4.67909227
H	3.82464242	-3.20042195	3.82923952
C	2.08843262	-2.74146580	2.62642062
C	4.64883683	1.26500219	-0.71300248
C	-0.73041733	3.50878412	1.48063267
C	-4.70344771	-1.29654076	-0.40345140
H	-0.13321185	4.33781335	1.84702553
C	-2.79983552	4.50479293	2.55508478
H	-3.87826457	4.33665967	2.59881367
H	-2.62179114	5.49657049	2.12659062
H	-2.41553802	4.52464703	3.58104023
C	-2.10553204	3.43893459	1.74882001

Total Energy = -1481.302791

**[Co(bpyMe<sub>2</sub>)<sub>2</sub>(CO<sub>2</sub>H)]<sup>+</sup>**

Co	-0.10822552	-0.35418555	-0.87278548
C	2.85130970	-0.89979707	2.21844715
C	2.08242631	-0.59608283	1.08994763
N	0.76725508	-0.88936496	1.03439520
C	0.19356144	-1.48306260	2.08768708
C	0.89373304	-1.81346707	3.24265601
C	3.96764794	0.46804704	-0.23867361
C	3.49793481	1.28593255	-2.43439676
C	2.18759716	0.86390751	-2.26143449
N	1.75775992	0.26902105	-1.13461589
C	2.63505256	0.06347886	-0.12171717
C	-2.14511115	1.40437561	0.13046158
N	-0.82118134	1.41223651	-0.15499925
C	-0.12317614	2.53440626	0.08368432
C	-4.19324676	-0.08083760	0.05495165
C	-3.95264757	-2.29062854	-0.80810195
C	-2.60596140	-2.02074732	-1.01099853
N	-2.03892180	-0.84130978	-0.69508439
C	-2.83235418	0.13018261	-0.17018917
C	-2.78453716	2.52594824	0.66364158
H	3.90734317	-0.65914117	2.24900994
H	-0.86671885	-1.69950449	1.99610795
H	0.37649283	-2.29202921	4.06794585
H	4.65751394	0.30628880	0.58045359
H	3.78710254	1.76428140	-3.36394940
H	1.44621009	1.00031732	-3.04177763
H	0.93299068	2.50318926	-0.15520964
H	-4.80161084	0.70902664	0.47826929
H	-4.34429312	-3.26523242	-1.07964923
H	-1.95357755	-2.76128145	-1.45258030
H	-3.84384994	2.49685063	0.88800873
C	0.37737919	-1.93692601	-1.83898458
O	1.28786046	-2.80377225	-1.29522094
O	-0.05683541	-2.17629163	-2.96400546
C	-6.25465479	-1.55030084	-0.04863536
H	-6.43300048	-2.55343003	0.34865251

H	-6.79124475	-1.47863955	-1.00197510
H	-6.68816716	-0.81812316	0.63608901
C	5.86505830	1.50573950	-1.55678692
H	5.94066561	2.47563890	-2.05621829
H	6.40703275	0.77933245	-2.17360883
H	6.36972189	1.56675532	-0.59002080
C	3.06532792	-1.87738736	4.54660882
H	3.20042394	-2.96295330	4.61278144
H	2.55049110	-1.56027571	5.45857069
H	4.05437451	-1.41451453	4.52570561
C	2.26199735	-1.52173795	3.32357343
C	4.42761244	1.08713458	-1.40456778
C	-0.69748698	3.68419149	0.60897162
C	-4.78536865	-1.30716134	-0.26128312
H	-0.07943658	4.55936705	0.77919026
C	-2.72837201	4.92633115	1.47536760
H	-3.76039220	4.72636636	1.77093706
H	-2.73546385	5.73062162	0.73133990
H	-2.18118359	5.29884124	2.34693099
C	-2.06497346	3.69803417	0.91339286
H	1.43559389	-3.49974880	-1.96558535
Total Energy = -1481.898066			

**[Co(bpyMe<sub>2</sub>)<sub>2</sub>(CO)]<sup>2+</sup>**

Co	-0.10689138	-0.16191103	-1.00915871
C	2.78446811	-1.60888054	1.80242062
C	2.05080229	-1.01379882	0.77448943
N	0.74328795	-1.29850021	0.58702460
C	0.14259381	-2.17209204	1.40583190
C	0.81302642	-2.80062762	2.44823920
C	3.95695467	0.36443766	-0.18619911
C	3.50267481	1.78423523	-2.05900141
C	2.18717910	1.35116950	-2.01749934
N	1.75259097	0.46595392	-1.10029329
C	2.62139182	-0.03950437	-0.18622598
C	-2.05744735	1.34502970	0.36045499
N	-0.72210315	1.34857218	0.10723305
C	0.02516354	2.34823614	0.60574179
C	-0.51432799	3.37779095	1.36432062
C	-4.14754706	-0.02377204	-0.05532395
C	-3.92462809	-2.05142246	-1.29705622
C	-2.56968487	-1.78175230	-1.41895369
N	-1.99723176	-0.68344161	-0.88979394
C	-2.78018061	0.19237790	-0.20394031
C	-2.65635945	2.35263491	1.11186917
H	3.83168194	-1.36963006	1.94112664
H	-0.90637375	-2.37169265	1.21442954
H	0.27974904	-3.50160404	3.08150225
H	4.64299478	-0.03991004	0.54756007
H	3.80141291	2.50248992	-2.81421407
H	1.44838512	1.71642841	-2.72228183
H	1.08446419	2.32088611	0.39124613
H	0.14143906	4.15426928	1.74209904
H	-4.75153620	0.69118042	0.48953989
H	-4.32510981	-2.95204910	-1.74870802
H	-1.92530786	-2.46604540	-1.95511935
H	-3.72221021	2.32801533	1.30207737
C	0.36981888	-1.45532184	-2.31574566
O	0.72232235	-2.22388945	-3.07291623
C	2.92653020	-3.17157413	3.79193488
H	3.99704050	-2.96690201	3.72767027
H	2.77569028	-4.25529876	3.78631217
H	2.56469637	-2.80000481	4.75710838
C	5.86431973	1.72168107	-1.15032436
H	6.40251585	1.37880609	-0.26479366
H	5.93942845	2.81148292	-1.20962553
H	6.36573597	1.31440405	-2.03545501
C	-2.51695327	4.51631297	2.41873092
H	-2.72671674	5.36667891	1.75907398

H	-1.84513658	4.87020994	3.20465246
H	-3.46096071	4.20441351	2.87069200
C	-6.22187686	-1.42464482	-0.43168761
H	-6.38336355	-2.07510093	0.43613364
H	-6.63541766	-1.93484918	-1.30497559
H	-6.77754403	-0.49986220	-0.26232399
C	-4.75275349	-1.16050590	-0.60368835
C	-1.88836264	3.40220419	1.63003408
C	4.42559903	1.28762280	-1.12672602
C	2.16895309	-2.52178486	2.66625359

Total Energy = -1405.920397

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