Supporting Information

Highly efficient and selective photocatalytic CO_2-to-CO conversion in aqueous solution

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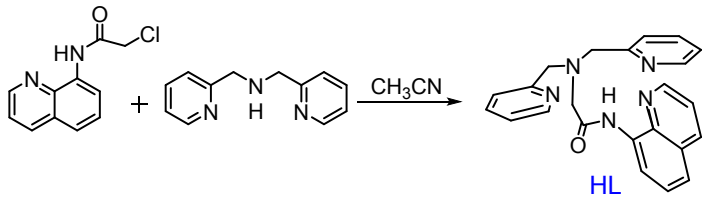
Contents

Experimental details

Materials and Methods

All reagents and solvents were purchased from commercial sources and were used without further purification. $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ and triethanolamine (TEOA) were purchased from Aldrich. Ultrapure water was prepared using a Hetai laboratory water purification system. The purities of carbon dioxide gas are 99.999% and 99% for $^{12}CO_2$ and $^{13}CO_2$, respectively. ^1H NMR measurements were performedon a Varian 400 MHz spectrometer and chemical shifts are recorded in ppm. X-ray diffraction data were collected on a Bruker APEX area-detector X-ray diffractometer. Mass spectra were obtained using a ThermoFinnigan LCQ DECA XP ion trap mass spectrometer. UV-Vis spectra were measured with a PerkinElmer LAMBDA 750 UV-vis-NIR spectrometer. The steady-state photoluminescence spectrum (PL) were collected using a Hitachi F-7000 Fluorescence spectrophotometer. The excitation wavelength was 430 nm. The irradiation experiments were conducted with a 5 W white LED light ($\lambda > 400$ nm, 90 mW cm^{-2}). Electrochemical measurements were carried out using an electrochemical workstation CHI 620E. The electrolyte was 0.1 M NBu_4PF_6 in CH_3CN solution. For cyclic voltammetric (CV) measurement, the reference electrode and the working electrode is Ag/AgCl (Saturated KCl) electrode and glassy carbon (GC) electrode, respectively. The potential of Ag/AgCl (Saturated KCl) reference electrode was calibrated using ferrocene/ferrocenium ($Fc^{0/+}$) as an external standard. The generated gas samples were analyzed by an Agilent 7820A gas chromatography equipped with a thermal conductivity detector (TCD) for the analysis of H_2 and a flame ionization detector (FID) for the analysis of CO. N_2 was used as the carrier gas. The oven temperature was held constant at 40 °C, and the inlet and detector temperature were set at 150 °C and 250 °C, respectively. Each photocatalytic reaction was repeated at least three times to confirm the reliability of the data.

Synthesis of the ligand HL



According to previously reported synthetic procedures,[1] ligand HL were synthesized, and showed identical spectroscopic properties to that reported therein. 2-Chloro-N-(quinolin-8-yl)acetamide (0.56 g, 2.54 mmol), bis((pyridin-2-yl)methyl)amine (0.5 g, 2.51 mmol), N,N-diisopropylethylamine (0.33 g, 2.58 mmol) and potassium iodide (0.46 g, 0.28 mmol) were dissolved in acetonitrile (40 mL), stirred and refluxed for 1 day under a

nitrogen atmosphere. The mixture was cooled to room temperature and the solvent was removed under reduced pressure to obtain a yellow solid, which was purified by silica gel column chromatography (45 : 1 *v*/*v* $CHCl_2$-CH_3OH). Yield: 0.60 g (62.5%). ^1H NMR (400 MHz, DMSO-d_6, 25 °C): δ = 11.43 (s, 1H), 9.05 (d, 1H), 8.61 (d, 1H), 8.48 (d, 2H), 8.42 (d, 1H), 7.87 (d, 2H), 7.78 (t, 2H), 7.67 (m, 2H), 7.56 (t, 1H), 7.24(t, 2H), 3.96 (s, 4H), 3.54 (s, 2H).

General synthesis of five complexes

The $M(ClO_4)_n$ (M = Co, Ni, Fe, Mn, Cu; n = 2 or 3, 0.031 mmol) solution in methanol (1 mL) was placed in a glass vial, respectively. Then the ligand HL (10.0 mg, 0.026 mmol) solution in methanol (1 mL) and triethylamine (0.0036 mL, 0.026 mmol) were added into above vials, respectively. The mixture was stirred for 30 min and allowed to stand overnight. The single crystals of five complexes suitable for X-ray crystallographic analysis were obtained. Yield: 87% for **1-Co**, 90% for **2-Ni**, 78% for **3-Fe**, 68% for **4-Mn**, and 85% for **5-Cu**. Elemental analysis data and ESI-MS of five complexes were obtained, respectively.

For $[Co(L)(OH)(ClO_4)]\cdot H_2O\cdot MeOH$: Calcd (%) for $C_{25}H_{30}ClN_5O_8Co$: C, 48.20; H, 4.85; N, 11.24. Found (%): C, 48.51; H, 4.77; N, 11.16. ESI-MS: *m*/*z* 474.03 for $[Co(L)(OH)]^+$.

For $[Ni(L)(ClO_4)]\cdot H_2O$: Calcd (%) for $C_{24}H_{25}ClN_5O_6Ni$: C, 50.25; H, 4.39; N, 12.21. Found (%): C, 50.04; H, 4.75; N, 11.87. ESI-MS: *m*/*z* 440.04 for $[Ni(dpaq)]^+$.

For $[Fe_2(L)_2(\mu_2\text{-}O)(ClO_4)_2]\cdot H_2O$: Calcd (%) for $C_{48}H_{48}Cl_2N_{10}O_{12}Fe_2$: C, 50.59; H, 4.25; N, 12.29. Found (%): C, 50.16; H, 4.58; N, 12.03. ESI-MS: *m*/*z* 455.17 for $[Fe(dpaq)(OH)]^+$.

For $[Mn(L)(OH)(ClO_4)]\cdot MeOH$: Calcd (%) for $C_{24}H_{25}ClN_5O_6Mn$: C, 50.58; H, 4.42; N, 12.29. Found (%): C, 50.42; H, 4.87; N, 12.01. ESI-MS: *m*/*z* 454.00 for $[Mn(dpaq)(OH)]^+$.

For $[Cu(L)(ClO_4)]\cdot MeOH$: Calcd (%) for $C_{24}H_{25}ClN_5O_6Cu$: C, 49.83; H, 4.36; N, 12.11. Found (%): C, 49.58; H, 4.82; N, 11.95. ESI-MS: *m*/*z* 445.04 for $[Cu(dpaq)]^+$.

X-ray crystallography

SCXRD data of five complexes were recorded on a Bruker APEX area-detector X-ray diffractometer with Mo-Kα radiation (λ = 0.71073 Å). The empirical absorption correction was performed by the SADABS program.[2] The structures were solved by direct method, and refined by full-matrix least-squares on F^2.[3] Crystallographic details are shown in Table S1 and S2, and Table S3-7 summarize the selected bond distances and angles. The CCDC numbers of **1-Co**, **2-Ni**, **3-Fe**, **4-Mn**, and **5-Cu** are 1955033-1955037, respectively.

Photocatalytic experiments and chromatographic detection of gases

A quartz container sealed with a rubber gasket was used as a photochemical cell. A typical procedure for the photocatalysis experiments was as follows: stock solutions with certain concentrations of the catalyst, photosensitizer and TEOA were initially prepared. Then, certain volumes of the stock solutions were added to a glass tube to give a sample with a total volume of 20.0 mL. The sample tube was sealed with a rubber septum, and then saturated by bubbling CO_2 gas for 50 min in the dark. Then the quartz container was put in the PCX50B Discover multi-channel parallel photocatalytic reaction system (Perfect Light) with a 5 W white LED light ($\lambda > 400$ nm, 90 mW cm^{-2}). The gas from headspace was extracted and analyzed by a gas chromatography every 1 hour during the photocatalysis. The generated gas samples were analyzed by an Agilent 7820A gas chromatography equipped with a thermal conductivity detector (TCD) for the analysis of H_2 and a flame ionization detector (FID) for the analysis of CO. N_2 was used as the carrier gas. The oven, inlet and detector temperatures were held constant at 40, 150 and 250 °C, respectively. Each photocatalytic reaction was repeated at least three times to confirm the reliability of the data.

$^{13}CO_2$ Labeling experiment

A 3 mL acetonitrile/water (*v*:*v* = 4:1) solution containing **1-Co** (0.15 μM), $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (0.5 mM) and TEOA (0.3 M) was purged with Ar for 15 min, followed by $^{13}CO_2$ bubbling for 30 min. The ^{13}CO generated during irradiation was detected by GC-MS (GC-2010 Pro, BID Detector).

The determination of quantum yield

Considering the fact that the reduction of CO_2 to CO is a two-electron process, the overall quantum yield of the process (Φ_{CO}) was calculated using the following equation:

$$\Phi_{CO} = \frac{\text{number of CO molecules} \times 2}{\text{number of protons absorbed}} \times 100$$

Based on the moles of CO in the sample headspace (obtained by GC measurements as described above) and Avogadro's number (6.022×10^{23}), the number of CO molecules was obtained. The number of photons absorbed was determined by measuring the incident light power inside the reaction vessel (90 mW cm^{-2}) (an PL-MW 2000 Photoradiometer was used). Taking the photon wavelength equal to 428 nm, and considering an illuminated area of 7.54 cm^2, the obtained quantum yield is obtained at 3 h of irradiation.

Electrochemistry study

Electrochemical experiments were performed with an electrochemical workstation CHI620E, using a glassy carbon working electrode (0.07 cm^2), a platinum wire auxiliary electrode, and an Ag/AgCl (Saturated KCl) reference electrode in 0.1 M NBu_4PF_6 solution acetonitrile/water (*v*:*v* = 4:1) solution at 25 ℃. All potentials were referenced against ferrocene/ferrocenium ($F_c^{0/+}$) as an external standard and converted to NHE by adding 0.124 V to the measured potentials. The glassy carbon electrode was polished with 0.05 μm Al_2O_3 slurry for 3 min to obtain a mirror surface, followed by sonication in distilled water for 5 min to remove debris and was thoroughly rinsed with ultrapure water. The electrolyte solution was saturated with Ar or CO_2 by purging with Ar or CO_2 for 15 min prior to each experiment.

Table S1 Crystal data and structure refinement for **1-Co, 2-Ni** and **3-Fe**.

Complex	**1-Co**	**2-Ni**	**3-Fe**
Formula	$C_{47}H_{40}Cl_2N_{10}O_{16}Co_2$	$C_{23}H_{20}ClN_5O_6Ni$	$C_{46}H_{40}Cl_2N_{10}O_{12}Fe_2$
F_w	1189.65	556.60	1107.48
cryst syst	monoclinic	monoclinic	monoclinic
space group	*C*2/c	$P2_1/n$	*C2/*c
a (Å)	16.718(3)	12.150(6)	15.885(8)
b (Å)	13.417(2)	13.633(7)	13.472(6)
c (Å)	22.998(4)	14.455(7)	23.262(10)
α (deg)	90	90	90
β (deg)	101.94(2)	107.636(8)	100.74(2)
γ (deg)	90	90	90
V (Å^3)	5046.8(15)	2281.9(19)	4891(4)
Z	4	4	4
D_c (g.cm^{-3})	1.566	1.620	1.504
F(000)	2432	1144	2272
μ (mm^{-1})	0.845	1.020	0.775
T (K)	296	296	296
reflns/unique	15504/5779	11474/4006	12602/4302
R_{int}	0.0402	0.1079	0.1310
data/restraints/params	5779/394/339	4006/373/334	4302/338/323
GOF on F^2	1.058	1.010	1.000
R_1, wR_2 ($I > 2\sigma(I)$)	0.0751, 0.2251	0.1071, 0.2637	0.0868, 0.2210
R_1, wR_2 (all data)	0.1082, 0.2523	0.1466, 0.3124	0.2025, 0.2960
largest diff. peak and hole (e.Å^{-3})	0.896, -0.645	1.446, -2.265	0.801, -0.646

Table S2 Crystal data and structure refinement for **4-Mn** and **5-Cu**.

Complex	**4-Mn**	**5-Cu**
Formula	$C_{24}H_{23}ClN_5O_6Mn$	$C_{48}H_{40}Cl_2N_{10}O_{12}Cu_2$
F_w	567.86	1146.88
cryst syst	orthorhombic	Triclinic
space group	$P2_12_12_1$	$P\bar{1}$
a (Å)	9.033(3)	13.82(3)
b (Å)	11.080(4)	14.61(4)
c (Å)	24.474(9)	14.99(4)
α (deg)	90	62.12(3)
β (deg)	90	76.15(4)
γ (deg)	90	71.48(4)
V (Å^3)	2450.0(15)	2522(11)
Z	4	2
D_c (g.cm^{-3})	1.540	1.510
F(000)	1168	1172
μ (mm^{-1})	0.699	1.021
T (K)	296	296
reflns/unique	15565/5665	12999/8741
R_{int}	0.0325	0.0646
data/restraints/params	5665/364/334	8741/0/647
GOF on F^2	1.024	0.933
R_1, wR_2 ($I > 2\sigma(I)$)	0.0546, 0.1573	0.0852, 0.2220
R_1, wR_2 (all data)	0.0694, 0.1702	0.1522, 0.2835
largest diff. peak and hole (e.Å^{-3})	0.862, -0.350	0.795, -0.829

Table S3 Selected Bond lengths [Å] and angles [º] for **1-Co**.

Co(1)-O(2)	1.873(4)	N(3)-Co(1)-N(5)	83.53(15)
Co(1)-N(2)	1.909(4)	O(2)-Co(1)-N(1)	103.33(16)
Co(1)-N(4)	1.946(4)	N(2)-Co(1)-N(1)	83.19(16)
Co(1)-N(3)	1.946(3)	N(4)-Co(1)-N(1)	95.70(15)
Co(1)-N(5)	1.946(3)	N(3)-Co(1)-N(1)	169.61(17)
Co(1)-N(1)	1.950(4)	N(5)-Co(1)-N(1)	96.30(15)
O(2)-Co(1)-N(2)	173.33(15)	C(1)-N(1)-Co(1)	128.9(4)
O(2)-Co(1)-N(4)	90.66(16)	C(5)-N(1)-Co(1)	112.2(3)
N(2)-Co(1)-N(4)	90.05(16)	C(10)-N(2)-Co(1)	117.9(3)
O(2)-Co(1)-N(3)	87.03(16)	C(6)-N(2)-Co(1)	115.3(3)
N(2)-Co(1)-N(3)	86.43(16)	C(11)-N(3)-Co(1)	108.7(3)
N(4)-Co(1)-N(3)	84.79(14)	C(12)-N(3)-Co(1)	106.9(3)
O(2)-Co(1)-N(5)	85.89(15)	C(18)-N(3)-Co(1)	107.4(2)
N(2)-Co(1)-N(5)	92.07(14)	C(17)-N(4)-Co(1)	127.8(3)
N(4)-Co(1)-N(5)	167.98(15)	C(13)-N(4)-Co(1)	112.9(3)

Table S4 Selected Bond lengths [Å] and angles [º] for **2-Ni**.

Ni(1)-N(2)	1.993(7)	N(4)-Ni(1)-O(1)	87.2(2)
Ni(1)-N(1)	2.075(6)	N(2)-Ni(1)-N(3)	83.1(2)
Ni(1)-N(5)	2.086(6)	N(1)-Ni(1)-N(3)	163.5(2)
Ni(1)-N(4)	2.089(6)	N(5)-Ni(1)-N(3)	81.5(2)
Ni(1)-O(1)	2.101(6)	N(4)-Ni(1)-N(3)	80.9(2)
Ni(1)-N(3)	2.111(6)	O(1)-Ni(1)-N(3)	98.9(2)
N(2)-Ni(1)-N(1)	80.5(2)	C(1)-N(1)-Ni(1)	128.9(5)
N(2)-Ni(1)-N(5)	90.1(2)	C(5)-N(1)-Ni(1)	111.6(5)
N(1)-Ni(1)-N(5)	97.3(2)	C(10)-N(2)-Ni(1)	118.8(5)
N(2)-Ni(1)-N(4)	95.7(2)	C(6)-N(2)-Ni(1)	116.2(5)
N(1)-Ni(1)-N(4)	101.8(2)	C(18)-N(3)-Ni(1)	106.7(4)
N(5)-Ni(1)-N(4)	160.7(2)	C(11)-N(3)-Ni(1)	107.0(4)
N(2)-Ni(1)-O(1)	176.7(2)	C(12)-N(3)-Ni(1)	106.9(4)
N(1)-Ni(1)-O(1)	97.5(2)	C(23)-N(5)-Ni(1)	129.9(5)
N(5)-Ni(1)-O(1)	87.7(2)	C(19)-N(5)-Ni(1)	111.9(5)

Table S5 Selected Bond lengths [Å] and angles [º] for **3-Fe**.

Fe(1)-O(1)	1.8093(16)	O(1)-Fe(1)-N(3)	103.1(2)
Fe(1)-N(2)	2.090(7)	N(2)-Fe(1)-N(3)	79.7(3)
Fe(1)-N(1)	2.094(8)	N(1)-Fe(1)-N(3)	155.9(3)
Fe(1)-N(5)	2.144(7)	N(5)-Fe(1)-N(3)	75.4(3)
Fe(1)-N(4)	2.182(7)	N(4)-Fe(1)-N(3)	77.4(3)

Fe(1)-N(3)	2.193(7)	Fe(1)-O(1)-Fe(1)#1	174.9(5)
O(1)-Fe(1)-N(2)	176.4(2)	C(10)-N(2)-Fe(1)	119.7(6)
O(1)-Fe(1)-N(1)	100.9(3)	C(6)-N(2)-Fe(1)	117.5(6)
N(2)-Fe(1)-N(1)	76.3(3)	C(11)-N(3)-Fe(1)	109.9(5)
O(1)-Fe(1)-N(5)	94.2(2)	C(12)-N(3)-Fe(1)	106.8(5)
N(2)-Fe(1)-N(5)	88.6(3)	C(18)-N(3)-Fe(1)	107.1(5)
N(1)-Fe(1)-N(5)	101.4(3)	C(17)-N(4)-Fe(1)	126.5(6)
O(1)-Fe(1)-N(4)	94.1(3)	C(13)-N(4)-Fe(1)	114.2(6)
N(2)-Fe(1)-N(4)	84.3(3)	C(19)-N(5)-Fe(1)	116.4(6)
N(1)-Fe(1)-N(4)	102.4(3)	C(23)-N(5)-Fe(1)	126.8(6)
N(5)-Fe(1)-N(4)	152.7(3)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1, y, -z+3/2

Table S6 Selected Bond lengths [Å] and angles [º] for **4-Mn.**

O(2)-Mn(1)-N(4)	101.25(19)	N(2)-Mn(1)-N(3)	88.62(18)
N(2)-Mn(1)-N(4)	82.28(17)	N(1)-Mn(1)-N(3)	95.75(16)
N(1)-Mn(1)-N(4)	160.80(18)	N(4)-Mn(1)-N(3)	76.56(16)
O(2)-Mn(1)-N(5)	85.82(18)	N(5)-Mn(1)-N(3)	152.02(17)
N(2)-Mn(1)-N(5)	89.12(17)	C(24)-N(1)-Mn(1)	127.9(4)
N(1)-Mn(1)-N(5)	111.29(17)	C(21)-N(1)-Mn(1)	113.1(3)
N(4)-Mn(1)-N(5)	75.50(17)	C(25)-O(2)-Mn(1)	129.2(5)
O(2)-Mn(1)-N(3)	98.20(19)	C(15)-N(2)-Mn(1)	120.1(4)
O(2)-Mn(1)-N(4)	101.25(19)	C(16)-N(2)-Mn(1)	117.6(3)
N(2)-Mn(1)-N(4)	82.28(17)	C(1)-N(3)-Mn(1)	126.7(4)
N(1)-Mn(1)-N(4)	160.80(18)	C(5)-N(3)-Mn(1)	114.9(3)
O(2)-Mn(1)-N(5)	85.82(18)	C(6)-N(4)-Mn(1)	109.1(3)
N(2)-Mn(1)-N(5)	89.12(17)	C(7)-N(4)-Mn(1)	108.0(3)
N(1)-Mn(1)-N(5)	111.29(17)	C(14)-N(4)-Mn(1)	106.3(3)
N(4)-Mn(1)-N(5)	75.50(17)	C(8)-N(5)-Mn(1)	114.5(4)
O(2)-Mn(1)-N(3)	98.20(19)	C(13)-N(5)-Mn(1)	127.3(4)
O(2)-Mn(1)-N(4)	101.25(19)		

Table S7 Selected Bond lengths [Å] and angles [º] for **5-Cu**.

Cu(1)-N(2)	1.906(8)	N(8)-Cu(2)-N(10)	80.7(3)
Cu(1)-N(1)	1.968(8)	N(9)-Cu(2)-N(10)	99.5(3)
Cu(1)-N(3)	2.013(8)	C(10)-N(2)-Cu(1)	119.5(6)
Cu(1)-N(4)	2.087(8)	C(6)-N(2)-Cu(1)	115.2(5)
Cu(1)-N(5)	2.100(8)	C(11)-N(3)-Cu(1)	106.0(5)
N(2)-Cu(1)-N(1)	82.9(3)	C(12)-N(3)-Cu(1)	104.9(5)
N(2)-Cu(1)-N(3)	83.3(3)	C(18)-N(3)-Cu(1)	109.6(6)

N(1)-Cu(1)-N(3)	165.3(3)	C(13)-N(4)-Cu(1)	109.4(6)
N(2)-Cu(1)-N(4)	128.5(3)	C(17)-N(4)-Cu(1)	131.0(7)
N(1)-Cu(1)-N(4)	103.7(3)	C(19)-N(5)-Cu(1)	113.2(6)
N(3)-Cu(1)-N(4)	81.2(3)	C(23)-N(5)-Cu(1)	130.2(6)
N(2)-Cu(1)-N(5)	123.5(3)	C(24)-N(6)-Cu(2)	129.6(6)
N(1)-Cu(1)-N(5)	110.1(3)	C(28)-N(6)-Cu(2)	111.2(5)
N(3)-Cu(1)-N(5)	81.9(3)	C(33)-N(7)-C(29)	125.3(7)
N(4)-Cu(1)-N(5)	102.3(3)	C(33)-N(7)-Cu(2)	119.1(5)
C(1)-N(1)-Cu(1)	129.7(6)	C(29)-N(7)-Cu(2)	115.4(5)
C(5)-N(1)-Cu(1)	112.5(6)	C(34)-N(8)-Cu(2)	107.3(5)
N(7)-Cu(2)-N(6)	83.4(3)	C(35)-N(8)-Cu(2)	104.5(5)
N(7)-Cu(2)-N(8)	83.0(3)	C(41)-N(8)-Cu(2)	108.4(5)
N(6)-Cu(2)-N(8)	165.9(3)	C(42)-N(9)-Cu(2)	111.3(6)
N(7)-Cu(2)-N(9)	125.0(3)	C(46)-N(9)-Cu(2)	130.8(6)
N(6)-Cu(2)-N(9)	106.8(3)	C(36)-N(10)-C(40)	118.3(8)
N(8)-Cu(2)-N(9)	84.2(3)	C(36)-N(10)-Cu(2)	110.9(5)
N(7)-Cu(2)-N(10)	130.4(3)	C(40)-N(10)-Cu(2)	130.7(6)
N(6)-Cu(2)-N(10)	105.5(3)		

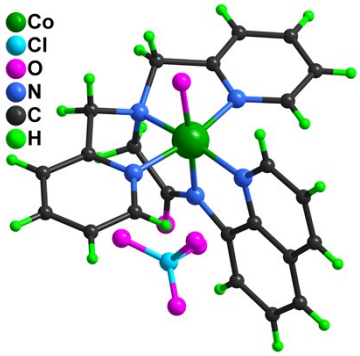


Fig. S1 X-ray diffraction structure of molecular catalyst **1-Co**.

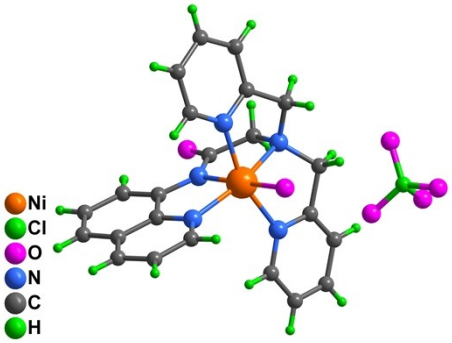


Fig. S2 X-ray diffraction structure of molecular catalyst **2-Ni**.

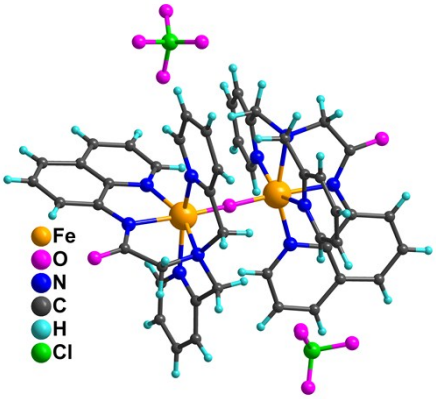


Fig. S3 X-ray diffraction structure of molecular catalyst **3-Fe**.

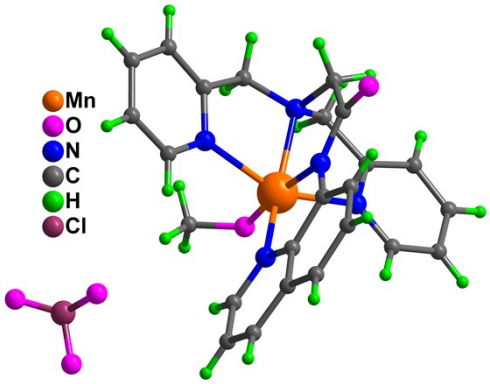


Fig. S4 X-ray diffraction structure of molecular catalyst **4-Mn**.

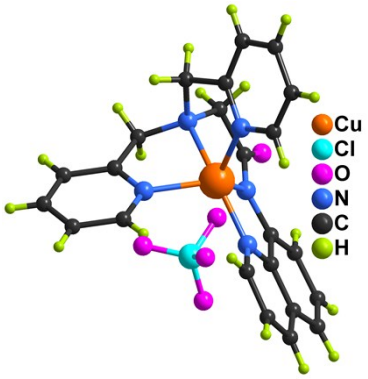


Fig. S5 X-ray diffraction structure of molecular catalyst **5-Cu**.

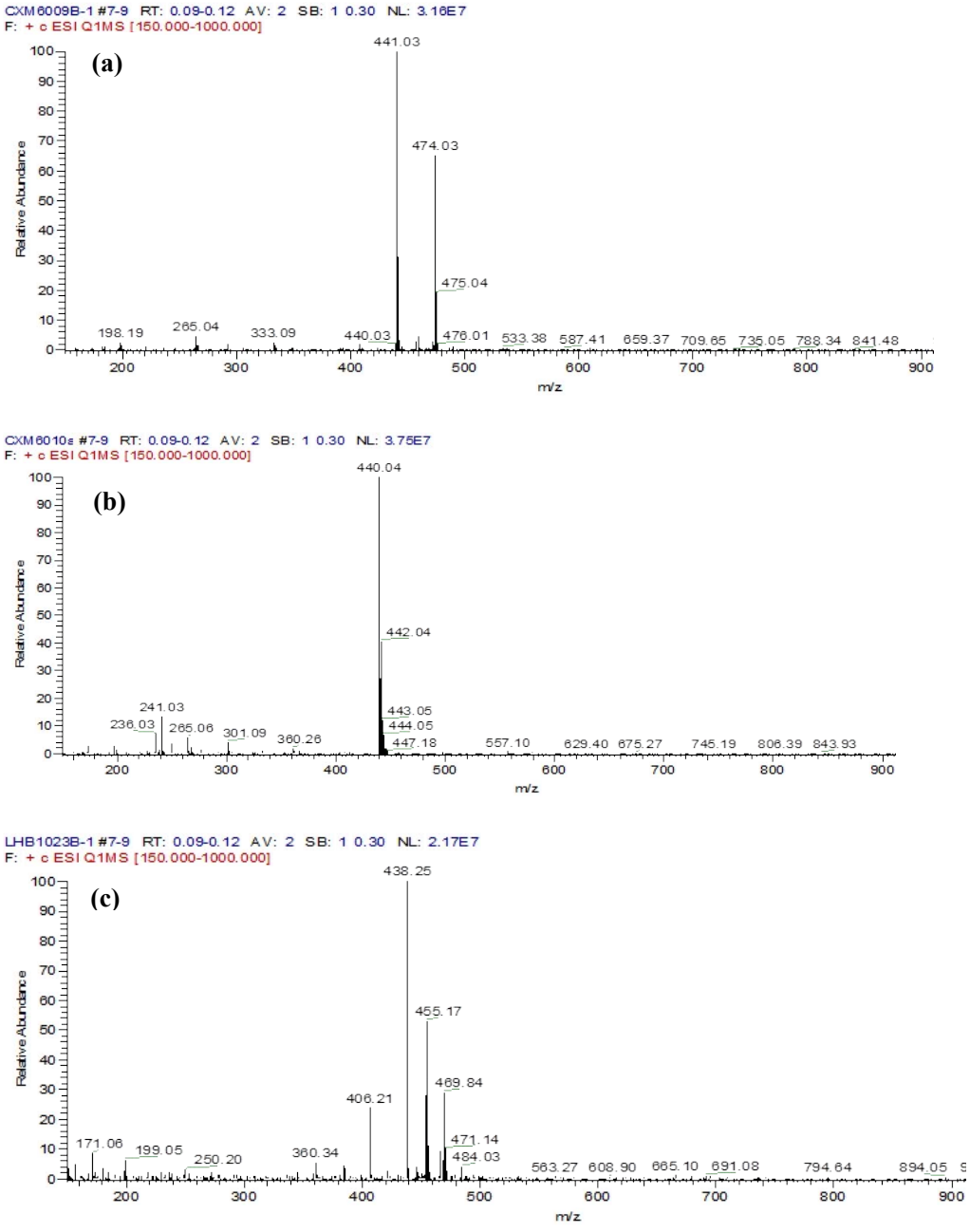


Fig. S6.1 ESI-MS of complexes **1-Co**(a), **2-Ni**(b), and **3-Fe**(c) in MeOH solution.

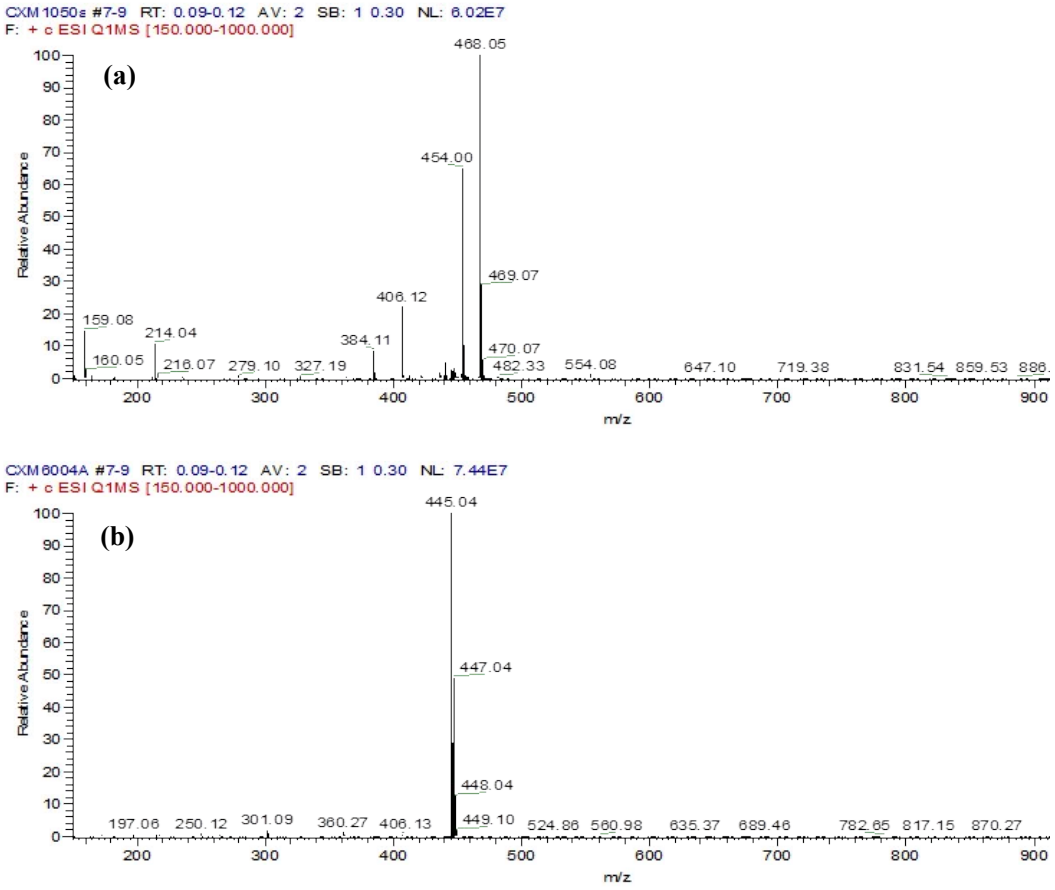


Fig. S6.2 ESI-MS of complexes **4-Mn**(a) and **5-Cu**(b) in MeOH solution.

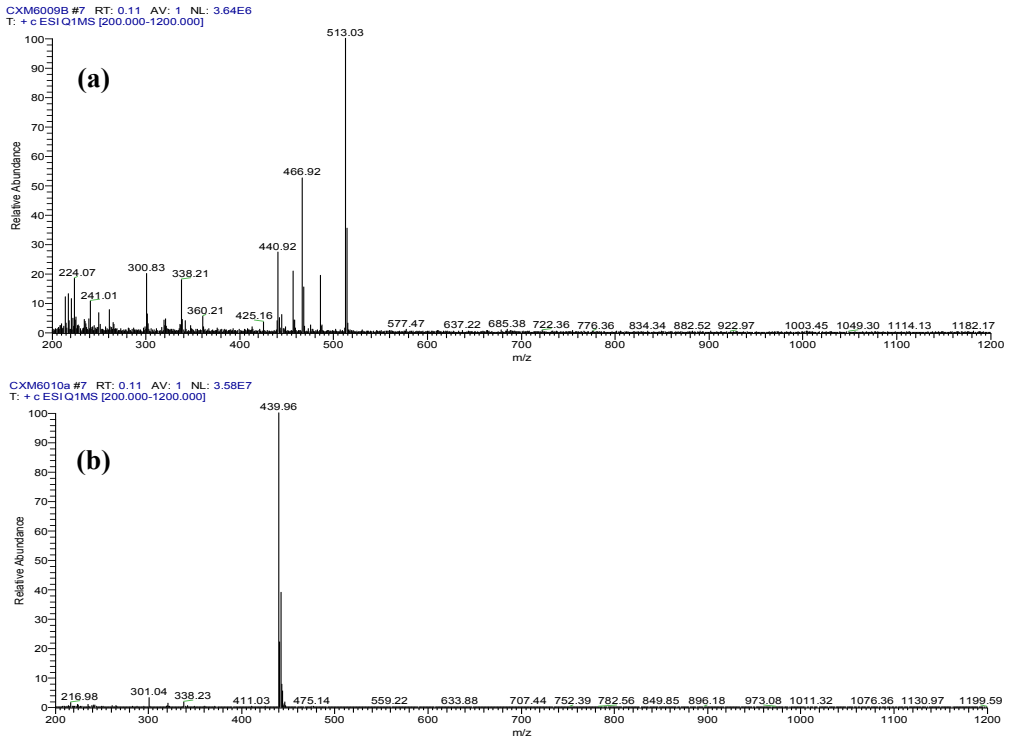


Fig. S7.1 ESI-MS of complexes **1-Co** (a), **2-Ni** (b) after conducting the photocatalytic CO formation in CH_3CN/H_2O (v:v = 4:1) solution for 3 h.

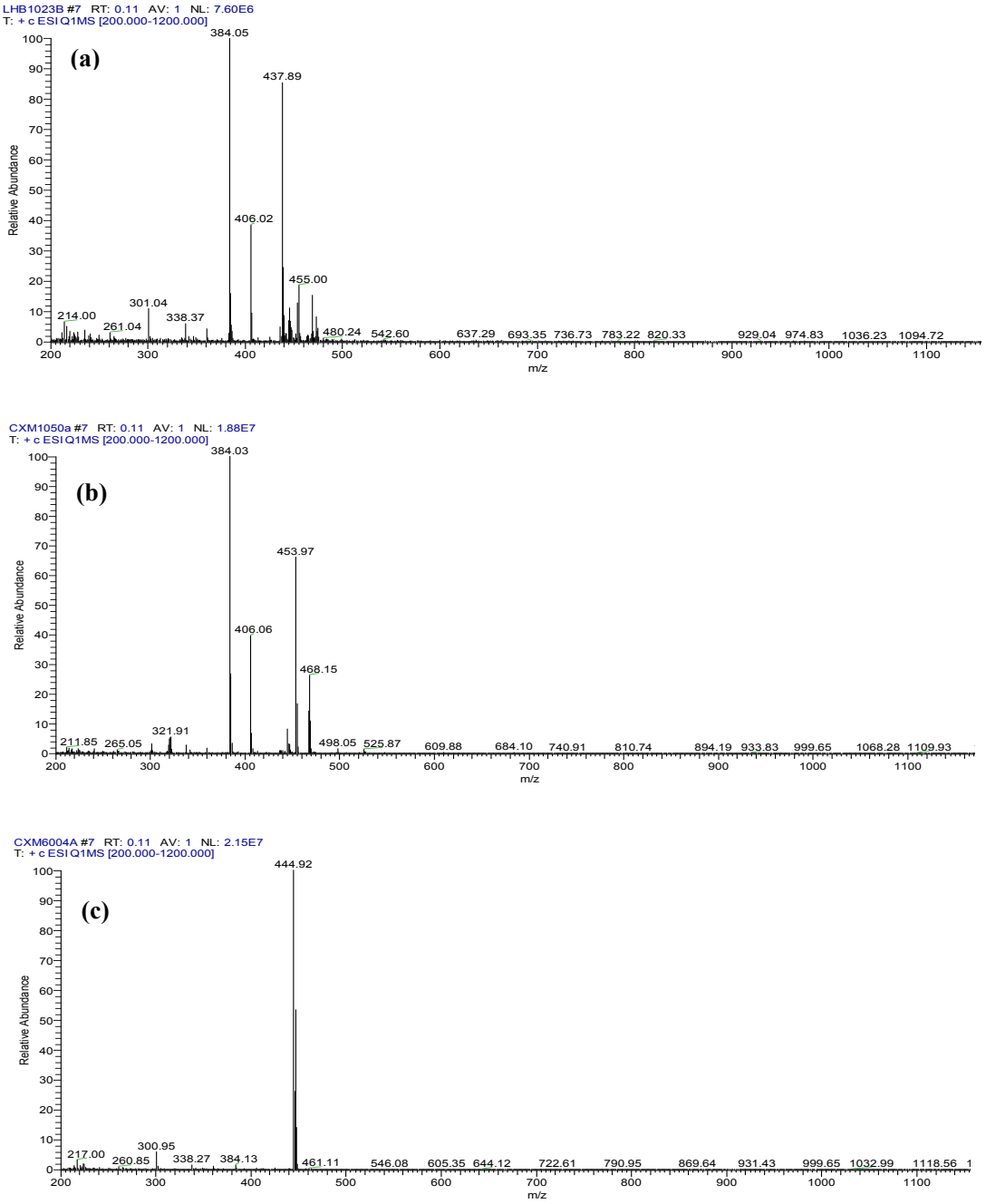


Fig. S7.2 ESI-MS of complexes **3-Fe** (a), **4-Mn** (b) and **5-Cu** (c) after conducting the photocatalytic CO formation in CH_3CN/H_2O (v:v = 4:1) solution for 3 h.

Table S8 Photoinduced CO_2 reduction catalyzed by **1-Co** under different control conditions.[a]

Entry	**1-Co** (μM)	CO (mmol)	H_2 (mmol)	TON for CO	TOF for CO (s^{-1})	CO selectivity (%)
1[b]	0.15	0.123	0.019	41017	3.80	87
2[c]	0	trace	trace	0	0	0
3[d]	0.15	0	0	0	0	0
4[e]	0.15	0	0	0	0	0
5[f]	0.15	0	0	0	0	0
6[g]	0.15	0	0.060	0	0	0

[a]Reaction conditions: $[Ru(bpy)_3]^{2+}$ (0.5 mM), TEOA (0.3 M), CH_3CN/H_2O (20 mL, *v*/*v*=4:1). LED light (λ>400 nm, 90 mW cm^{-2}, irradiation area 7.54 cm^2), 25 °C, 3 h. [b]100 % CO_2. [c]Without **1-Co**. [d]Without $[Ru(bpy)_3]^{2+}$. [e]Without TEOA. [f]Without light. [g]100 % Ar.

Table S9.1 Results of photocatalytic CO_2 reduction under different concentrations of **1-Co**.

Catalyst (μM)	CO (mmol)	H_2 (mmol)	TON for CO	TOF for CO (s^{-1})	selectivity to CO (%)	Φ (%)
0.075	0.076	0.012	50839	4.71	86	0.58
0.1	0.095	0.013	47706	4.42	88	0.73
0.125	0.113	0.013	45333	4.20	89	0.86
0.15	0.123	0.019	41017	3.80	87	0.94
0.2	0.159	0.026	39843	3.69	86	1.21
0.25	0.199	0.030	39818	3.68	87	1.52
0.3	0.228	0.033	38011	3.52	87	1.74

Reaction conditions: catalyst **1-Co**, $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (0.5 mM), TEOA (0.3 M), White LED light (λ > 400 nm, irradiation area 7.54 cm^2), 25 ˚C, 3 h.

Table S9.2 Some representative results of previously reported homogeneous photocatalysts toward CO_2-to-CO conversion.

Catalyst (μM)	CO (μmol)	TON	TOF (s^{-1})	Time (h)	Solvent	Ref.
CAT1-Re (100)	10	50	0.0139	1	CH_3CN	4
CAT2-Re (50)	19.68	98	0.0018	15	DMF	5
CAT3-Ru (2)	220	110	0.0153	2	DMF	6
CAT4-Ru (100)	82	164	0.018	5	DMA/H_2O	7
CAT5-Ir (500)	100	50	2.7×10^{-4}	5	DMF	8
CAT6-Ir (500)	530	265	4.17×10^{-4}	200	CH_3CN	9
CAT7-Mn (100)	0.038	19	3.52×10^{-4}	15	CH_3CN	10
CAT8-Fe (2)	1.386	198	0.0012	47	CH_3CN	11
CAT9-Fe (2)	2.5	367	0.001	102	CH_3CN	12
CAT10-Ni (2×10^{-3})	1.96	98000	3.9	7	CH_3CN	13
CAT10-Ni (0.2)	3.0	1500	0.058	7	CH_3CN	13
CAT11-Ni (30)	86	713	0.0036	55	DMA/H_2O	14
CAT12-Cu (1)	31.2	12400	1.14	3	H_2O/ CH_3CN	15
CAT13-Cu (0.05)	2.48	9900	0.275	10	H_2O/CH_3CN	16

CAT14-Co (0.05)	2.9	11600	0.32	10	H_2O/CH_3CN	17
CAT15-Co (0.05)	0.4	1600	0.04	10	H_2O/CH_3CN	17
CAT16-Co (0.05)	3.17	12680	0.35	10	H_2O/CH_3CN	18
CAT17-Co (0.05)	2.82	11280	0.31	10	H_2O/CH_3CN	18
CAT18-Co (5)	135	2680	0.186	4	$NaHCO_3$ buffer	19
CAT19-Co (10)	92.6	926	0.127	4	$NaHCO_3$ buffer	20
CAT20-Co (5)	27	2660	0.097	1.3	CH_3CN	21
CAT21-CoCo (0.025)[a]	2.11	17000	0.47	10	H_2O/CH_3CN	22
CAT22-CoZn (0.025)[a]	8.10	65000	1.8	10	H_2O/CH_3CN	23
CAT23-ZnZn (0.025)	0.42	3400	0.093	10	H_2O/CH_3CN	23
1-Co (0.075)	76	50839	4.71	3	H_2O/CH_3CN	This work
1-Co (0.15)	123	41017	3.80	3	H_2O/CH_3CN	This work
1-Co (0.3)	228	38011	3.52	3	H_2O/CH_3CN	This work

a: The synergistic catalysis between two metal sites were observed in the two photocatalytic processes.

Table S10 The results of photocatalytic CO_2 reduction catalyzed by five catalysts under the same conditions.[a]

Catalyst	CO (mmol)	H_2 (mmol)	TON for CO	TOF for CO (s^{-1})	selectivity to CO (%)
1-Co	0.123	0.019	41017	3.80	87
2-Ni	0.114	0.019	37854	3.51	86
3-Fe	0.054	0.015	18138	1.68	78
4-Mn	0.037	0.013	12350	1.14	74
5-Cu	0.027	0.012	9109	0.84	69

[a]Reaction conditions: five catalysts (0.15 μM), $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (0.5 mM), TEOA (0.3 M), CH_3CN/H_2O (20 mL, *v*/*v* = 4:1). White LED light (λ > 400 nm, 90 mW cm^{-2}, irradiation area 7.54 cm^2), 25 °C, 3 h.

Table S11.1 Photoinduced CO_2 reduction catalyzed by **2-Ni** under different conditions.[a]

Entry	**2-Ni** (μM)	CO (mmol)	H_2 (mmol)	TON for CO	TOF for CO(s^{-1})	CO selectivity (%)
1[b]	0.15	0.114	0.019	37854	3.51	86
2[c]	0	trace	trace	0	0	0
3[d]	0.15	0	0	0	0	0
4[e]	0.15	0	0	0	0	0
5[f]	0.15	0	0	0	0	0
6[g]	0.15	0	0.025	0	0	0

[a]Reaction conditions: $[Ru(bpy)_3]^{2+}$ (0.5 mM), TEOA (0.3 M), CH_3CN/H_2O (20 mL, *v*/*v* = 4:1). LED light (λ > 400 nm, 90 mW cm^{-2}, irradiation area 7.54 cm^2), 25 °C, 3 h. [b]100 % CO_2. [c]Without **2-Ni**. [d]Without $[Ru(bpy)_3]^{2+}$. [e]Without TEOA. [f]Without light. [g]100 % Ar.

Table S11.2 Photoinduced CO_2 reduction catalyzed by **3-Fe** under different conditions.[a]

Entry	**3-Fe** (μM)	CO (mmol)	H_2 (mmol)	TON for CO	TOF for CO(s^{-1})	CO selectivity (%)
1[b]	0.15	0.054	0.015	18138	1.68	78
2[c]	0	trace	trace	0	0	0
3[d]	0.15	0	0	0	0	0
4[e]	0.15	0	0	0	0	0
5[f]	0.15	0	0	0	0	0
6[g]	0.15	0	0.027	0	0	0

[a]Reaction conditions: $[Ru(bpy)_3]^{2+}$ (0.5 mM), TEOA (0.3 M), CH_3CN/H_2O (20 mL, *v*/*v* = 4:1). LED light (λ > 400 nm, 90 mW cm^{-2}, irradiation area 7.54 cm^2), 25 °C, 3 h. [b]100 % CO_2. [c]Without **3-Fe**. [d]Without $[Ru(bpy)_3]^{2+}$. [e]Without TEOA. [f]Without light. [g]100 % Ar.

Table S11.3 Photoinduced CO_2 reduction catalyzed by **4-Mn** under different conditions.[a]

Entry	**4-Mn** (μM)	CO (mmol)	H_2 (mmol)	TON for CO	TOF for CO(s^{-1})	CO selectivity (%)
1[b]	0.15	0.037	0.013	12350	1.14	74
2[c]	0	trace	trace	0	0	0
3[d]	0.15	0	0	0	0	0
4[e]	0.15	0	0	0	0	0
5[f]	0.15	0	0	0	0	0
6[g]	0.15	0	0.029	0	0	0

[a]Reaction conditions: $[Ru(bpy)_3]^{2+}$ (0.5 mM), TEOA (0.3 M), CH_3CN/H_2O (20 mL, *v*/*v* = 4:1). LED light (λ > 400 nm, 90 mW cm^{-2}, irradiation area 7.54 cm^2), 25 °C, 3 h. [b]100 % CO_2. [c]Without **4-Mn**. [d]Without $[Ru(bpy)_3]^{2+}$. [e]Without TEOA. [f]Without light. [g]100 % Ar.

Table S11.4 Photoinduced CO_2 reduction catalyzed by **5-Cu** under different conditions.[a]

Entry	**5-Cu** (μM)	CO (mmol)	H_2 (mmol)	TON for CO	TOF for CO(s^{-1})	CO selectivity (%)
1[b]	0.15	0.027	0.012	9109	0.84	69
2[c]	0	trace	trace	0	0	0
3[d]	0.15	0	0	0	0	0
4[e]	0.15	0	0	0	0	0
5[f]	0.15	0	0	0	0	0
6[g]	0.15	0	0.011	0	0	0

[a]Reaction conditions: $[Ru(bpy)_3]^{2+}$ (0.5 mM), TEOA (0.3 M), CH_3CN/H_2O (20 mL, *v*/*v* = 4:1). LED light (λ > 400 nm, 90 mW cm^{-2}, irradiation area 7.54 cm^2), 25 °C, 3 h. [b]100 % CO_2. [c]Without **5-Cu**. [d]Without $[Ru(bpy)_3]^{2+}$. [e]Without TEOA. [f]Without light. [g]100 % Ar.

Table S12.1 Results of photocatalytic CO_2 reduction by changing the ratio of $[Ru(bpy)_3]^{2+}$ to **1-**

Co.

Catalyst	PS	CO (mmol)	H_2 (mmol)	TON for CO	TOF for CO (s^{-1})	selectivity to CO (%)
1-Co[a] (0.15 μM)	$[Ru(bpy)_3]Cl_2·6H_2O$ (0.5 mM)	0.123	0.019	41017	3.80	87
1-Co[b] (0.15 mM)	$[Ru(bpy)_3]Cl_2·6H_2O$ (0.15 mM)	0.126	0.014	42	0.004	90

Reaction conditions: [a]**1-Co** (0.15 μM), $[Ru(bpy)_3]Cl_2·6H_2O$ (0.5 mM), TEOA (0.3 M), White LED light (λ > 400 nm, irradiation area 7.54 cm^2), 25 ˚C, 3 h. [b]**1-Co** (0.15 mM), $[Ru(bpy)_3]Cl_2·6H_2O$ (0.15 mM), TEOA (0.3 M), White LED light (λ > 400 nm, irradiation area 7.54 cm^2), 25 ˚C, 3 h.

Table S12.2 Results of photocatalytic CO_2 reduction under the different photosensitizer concentrations.

PS (mM)	CO (mmol)	H_2 (mmol)	TON for CO	TOF for CO (s^{-1})	selectivity to CO (%)	Φ (%)
0.5	0.123	0.019	41017	3.80	87	0.94
0.4	0.120	0.019	40040	3.71	86	0.92
0.3	0.092	0.011	30569	2.83	89	0.70
0.2	0.058	0.008	19358	1.79	88	0.44

Reaction conditions: catalyst **1-Co** (0.15 μM), $[Ru(bpy)_3]Cl_2·6H_2O$, TEOA (0.3 M), White LED light (λ > 400 nm, irradiation area 7.54 cm^2), 25 ˚C, 3 h.

Table S13 The experimental results for photocatalytic reduction of CO_2 to CO by **1-Co** with different light intensities.[a]

LED light (%)	Light intensity (mW cm^{-2})	CO (mmol)	H_2 (mmol)	TON for CO	TOF for CO (s^{-1})	selectivity to CO (%)
100	90	0.123	0.019	41017	3.80	87
90	82	0.120	0.025	40000	3.70	83
80	75	0.118	0.024	39333	3.64	83
70	66	0.112	0.020	37333	3.46	85

[a]Reaction conditions: **1-Co** (0.15 μM), $[Ru(bpy)_3]Cl_2·6H_2O$ (0.5 mM), TEOA (0.3 M), White LED light (λ > 400 nm, irradiation area 7.54 cm^2), 25 ˚C, 3 h.

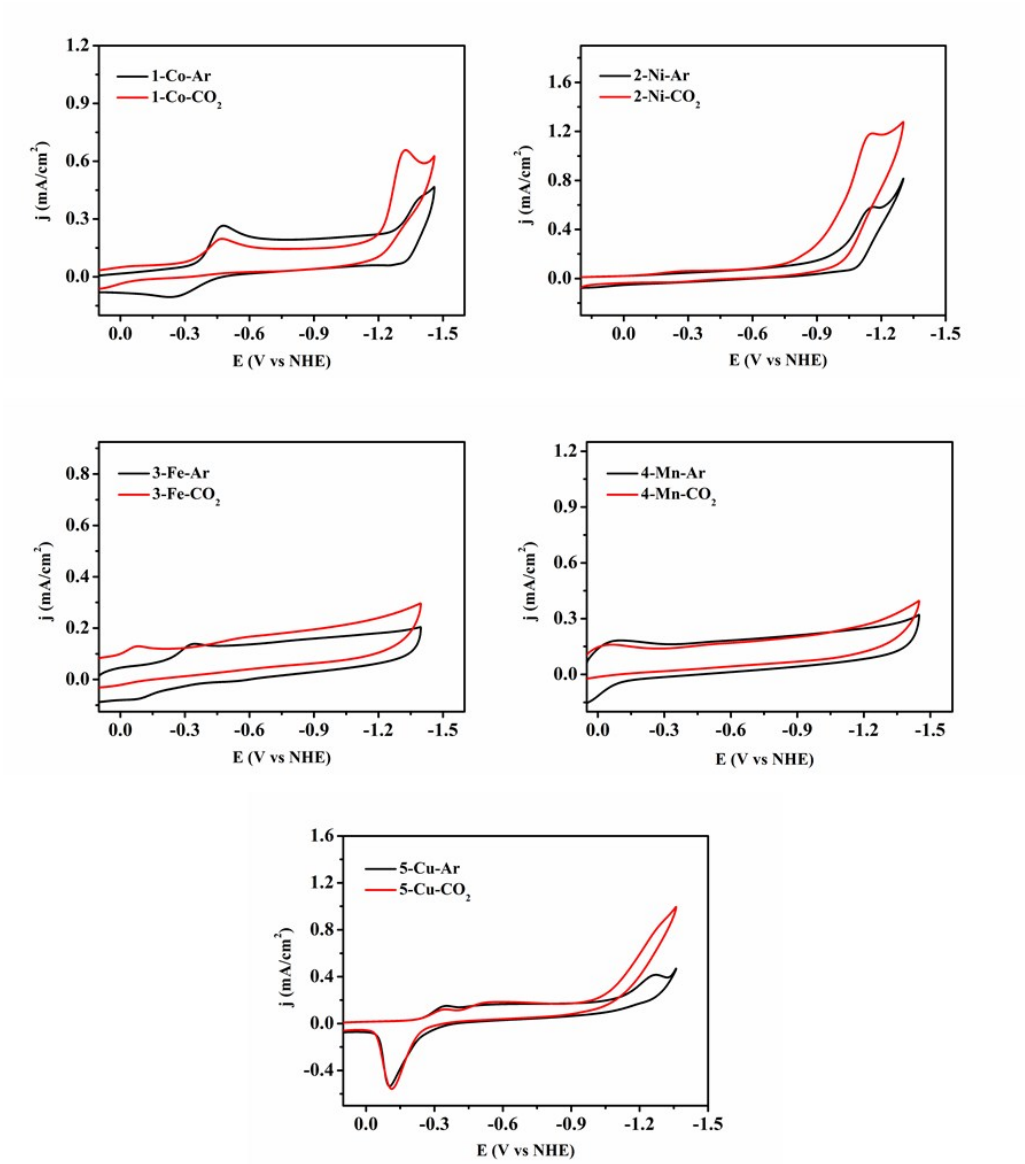


Fig. S8 CV curves of five complexes (0.5 mM) in CH_3CN/H_2O (v:v = 4:1) solution containing 0.1 M NBu_4PF_6 under an Ar (black) and CO_2 atmosphere (red).

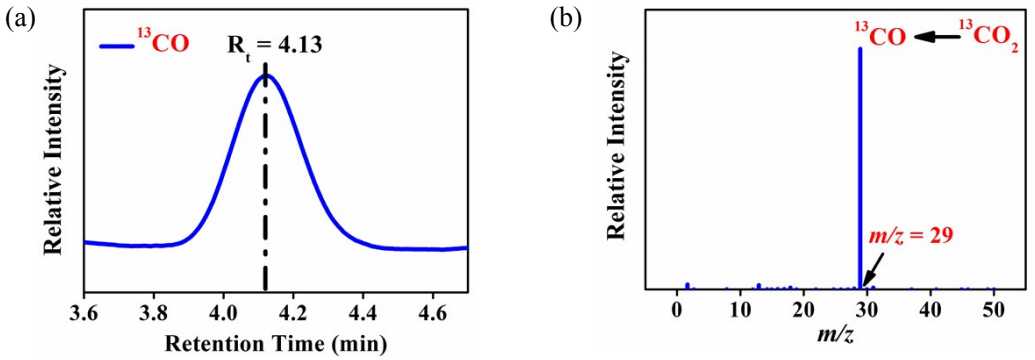


Fig. S9 Gas chromatogram (a) and mass spectrum (b) of ^{13}CO produced from the photocatalytic reduction of $^{13}CO_2$ using Co-based catalyst **1-Co**.

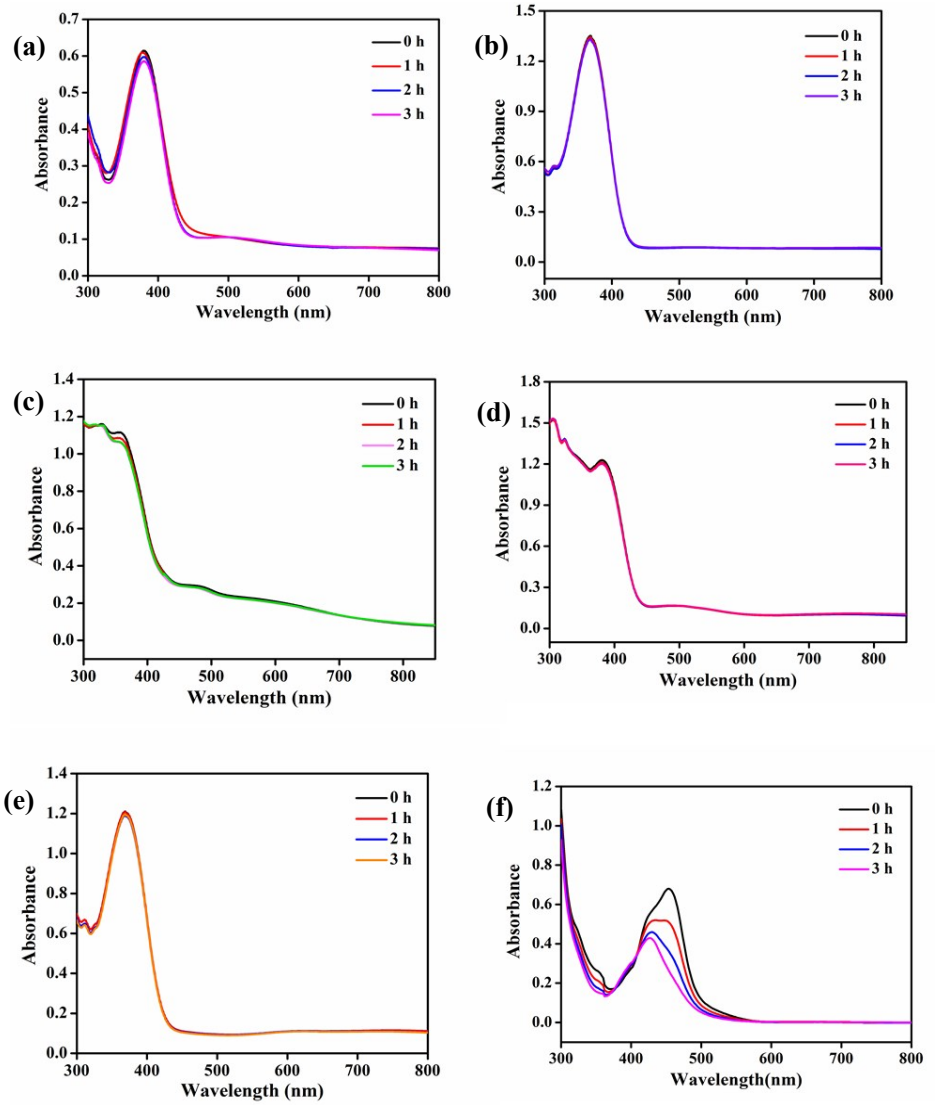


Fig. S10 UV-Vis absorbance of (a) 0.1 mM catalyst **1-Co**, (b) 0.2 mM catalyst **2-Ni**, (c) 0.2 mM catalyst **3-Fe**, (d) 0.2 mM catalyst **4-Mn**, (e) 0.2 mM catalyst **5-Cu** and (f) 0.05 mM $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ in CH_3CN/H_2O (*v*:*v* = 4:1) after irradiation for 0, 1, 2 and 3 h with white LED light.

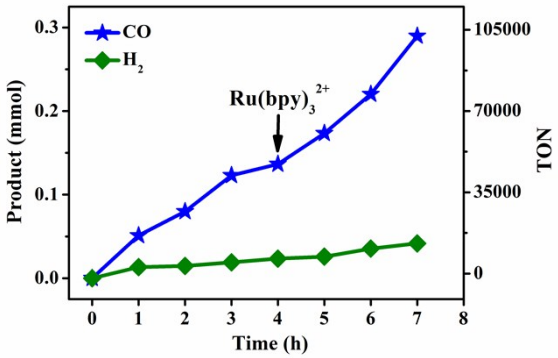


Fig. S11 The ceased CO_2-to-CO conversion catalyzed by **1-Co** was resumed upon the addition of fresh equivalent of $[Ru(bpy)_3]^{2+}$ (0.5 mM).

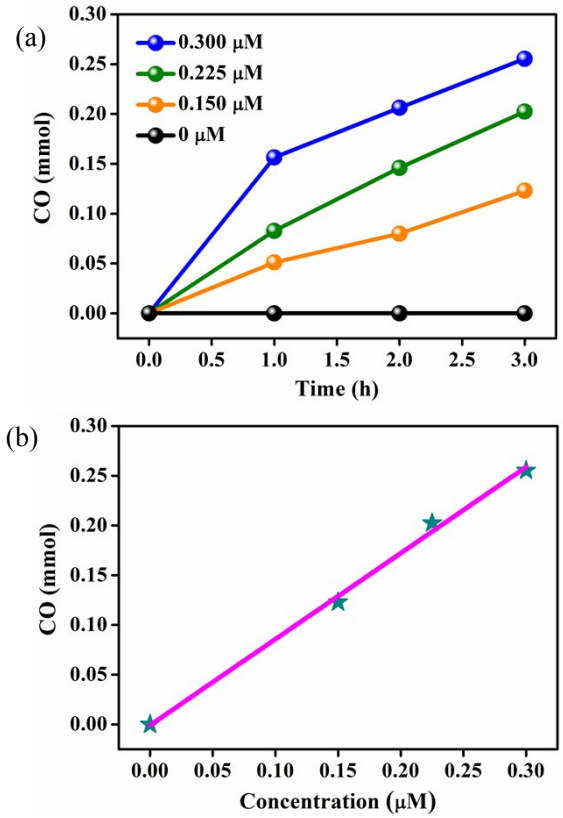


Fig. S12 (a) CO evolution with different concentrations of **1-Co**. Conditions: λ > 400 nm LED light, 0.5 mM $[Ru(bpy)_3]^{2+}$, 0.3 M TEOA, 20 mL CO_2-saturated acetonitrile/water (*v*:*v*= 4:1). (b) The amounts of CO evolution at 3 h *vs* the concentrations of **1-Co** (y = 0.86543x– 8.2784× 10^{-4}, R^2 = 0.995).

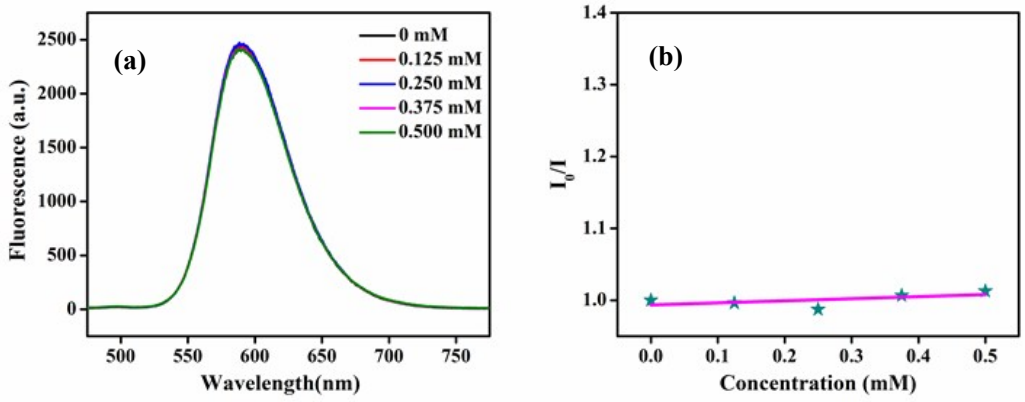


Fig. S13 (a) Fluorescence spectra of an acetonitrile/water (*v*:*v* = 4:1) solution containing 0.05 mM $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ in the absence (black) and presence of 0.125 mM, 0.250 mM, 0.375 mM and 0.5 mM TEOA. (b) Linear plot of ratio of fluorescence intensity in the absence and presence of TEOA versus the concentration of TEOA.

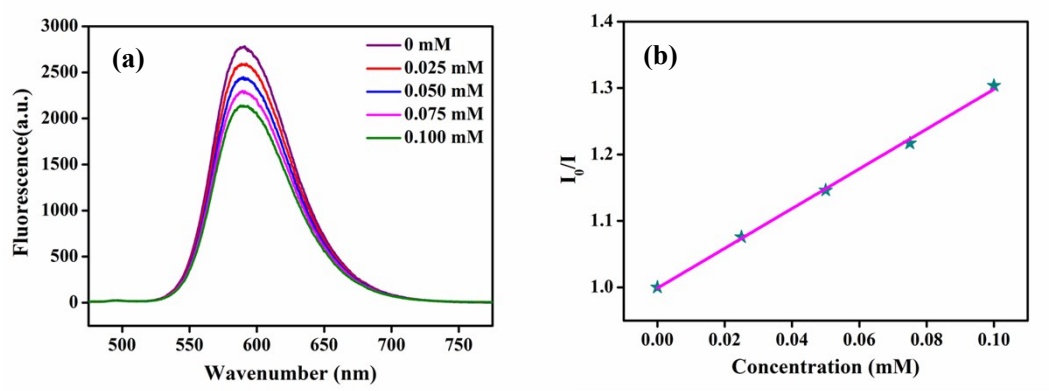


Fig. S14.1 (a) Fluorescence spectra of an acetonitrile/water (*v*:*v* = 4:1) solution containing 0.05 mM $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ in the absence (black) and presence of 0.025 mM, 0.050 mM, 0.075 mM and 0.100 mM **1-Co**. (b) Linear plot of ratio of fluorescence intensity in the absence and presence of **1-Co** versus the concentration of **1-Co** (R^2 = 0.998).

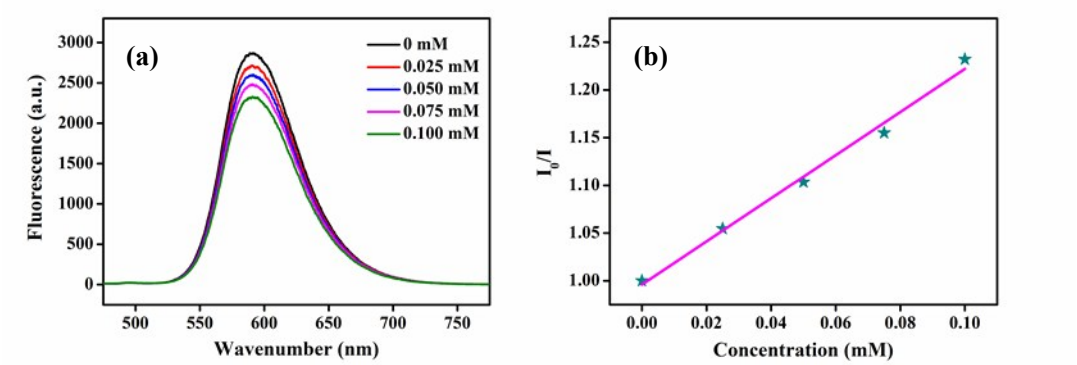


Fig. S14.2 (a) Fluorescence spectra of an acetonitrile/water (*v*:*v* = 4:1) solution containing 0.05 mM $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ in the absence (black) and presence of 0.025 mM, 0.050 mM, 0.075 mM and 0.100 mM **2-Ni**. (b) Linear plot of ratio of fluorescence intensity in the absence and presence of **2-Ni** versus the concentration of **2-Ni** (R^2 = 0.989).

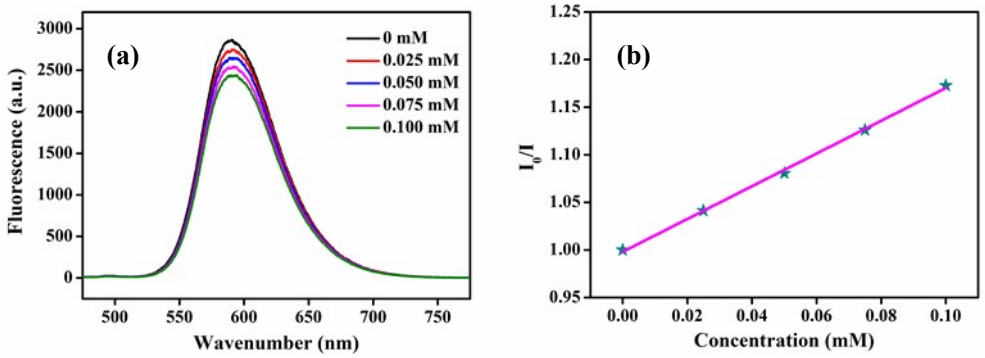


Fig. S14.3 (a) Fluorescence spectra of an acetonitrile/water (*v*:*v* = 4:1) solution containing 0.05 mM $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ in the absence (black) and presence of 0.025 mM, 0.050 mM, 0.075 mM and 0.100 mM **3-Fe**. (b) Linear plot of ratio of fluorescence intensity in the absence and presence of **3-Fe** versus the concentration of **3-Fe** (R^2 = 0.998).

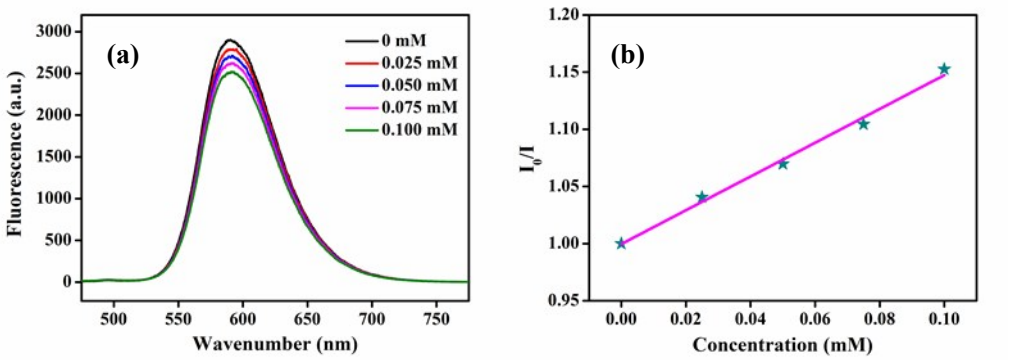


Fig. S14.4 (a) Fluorescence spectra of an acetonitrile/water (*v*:*v* = 4:1) solution containing 0.05 mM $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ in the absence (black) and presence of 0.025 mM, 0.050 mM, 0.075 mM and 0.100 mM **4-Mn**. (b) Linear plot of ratio of fluorescence intensity in the absence and presence of **4-Mn** versus the concentration of **4-Mn** (R^2 = 0.991).

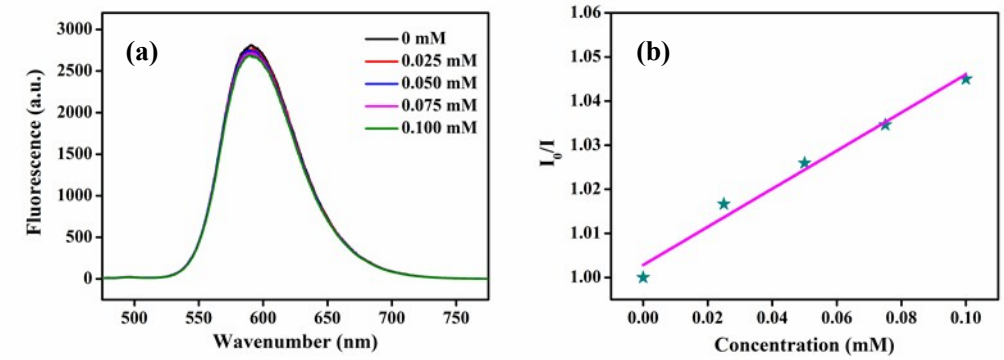


Fig. S14.5 (a) Fluorescence spectra of an acetonitrile/water (*v*:*v* = 4:1) solution containing 0.05 mM $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ in the absence (black) and presence of 0.025 mM, 0.050 mM, 0.075 mM and 0.100 mM **5-Cu**. (b) Linear plot of ratio of fluorescence intensity in the absence and presence of **5-Cu** versus the concentration of **5-Cu** (R^2 = 0.976).

To determine whether the excited state of photosensitizer is quenched by catalyst or sacrificial electron donor, fluorescence quenching experiments were conducted based on the Stern−Volmer equation:

$$\frac{I_0}{I} = 1+k_q\tau_0[Q]$$

where I_0/I is the fluorescence intensity in the absence/presence of quencher, k_q is the apparent rate of quenching, τ_0 is the lifetime of the excited state and [Q] is the concentration of quencher.

To determine the apparent quenching rate (kq), the lifetime changes of [Ru(phen)3]* in the absence and presence of 1 were measured according to the Stern−Volmer equation:

$$\frac{\tau_0}{\tau} = 1+k_q\tau_0[Q]$$

Where τ_0 and τ are the lifetimes of the excited state in the absence and presence of quencher Q respectively.

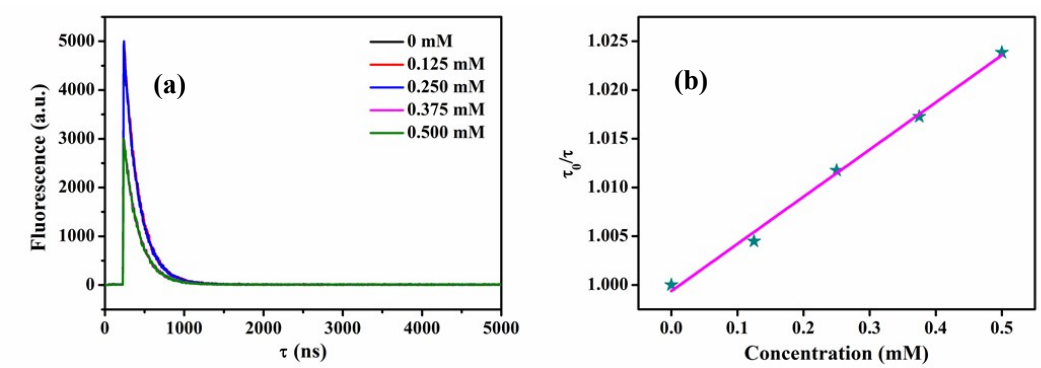


Fig. S15.1 (a) Fluorescence lifetime of 0.05 mM $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ acetonitrile/water (*v*:*v* = 4:1) solution in the presence of 0 mM (black), 0.125 mM (red), 0.250 mM (blue), 0.375 mM (magenta) and 0.5 mM (olive) of **1-Co**. (b) τ_0/τ versus the concentration of catalyst **1-Co**, in agreement with the Stern–Volmer equation (y = 2.99396x + 1, R^2 = 0.9988).

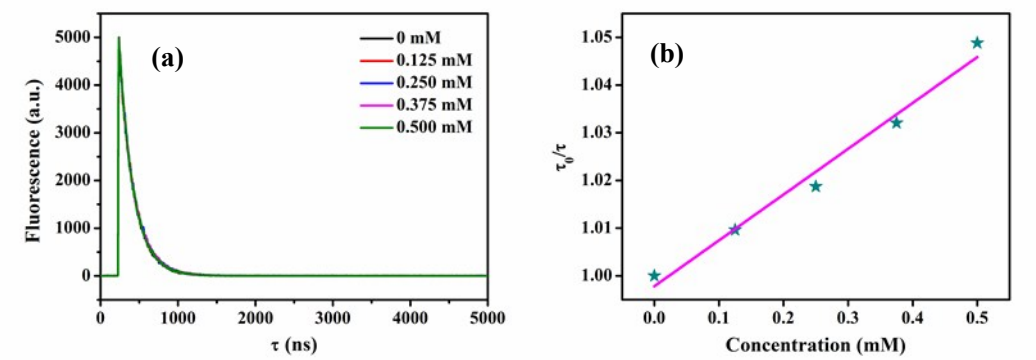


Fig. S15.2 (a) Fluorescence lifetime of 0.05 mM $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ acetonitrile/water (*v*:*v* = 4:1) solution in the presence of 0 mM (black), 0.125 mM (red), 0.250 mM (blue), 0.375 mM (magenta) and 0.5 mM (olive) of **2-Ni**. (b) τ_0/τ versus the concentration of catalyst **2-Ni**, in agreement with the Stern–Volmer equation (y = 1.72134x + 1, R^2 = 0.9981).

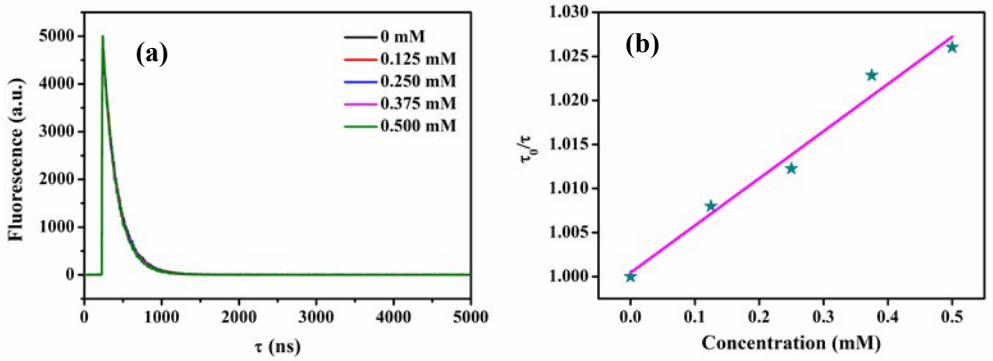


Fig. S15.3 (a) Fluorescence lifetime of 0.05 mM $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ acetonitrile/water (*v*:*v* = 4:1) solution in the presence of 0 mM (black), 0.125 mM (red), 0.250 mM (blue), 0.375 mM (magenta) and 0.5 mM (olive) of **3-Fe**. (b) τ_0/τ versus the concentration of catalyst **3-Fe**, in agreement with the Stern–Volmer equation (y = 2.2594x + 1, R^2 = 0.9961).

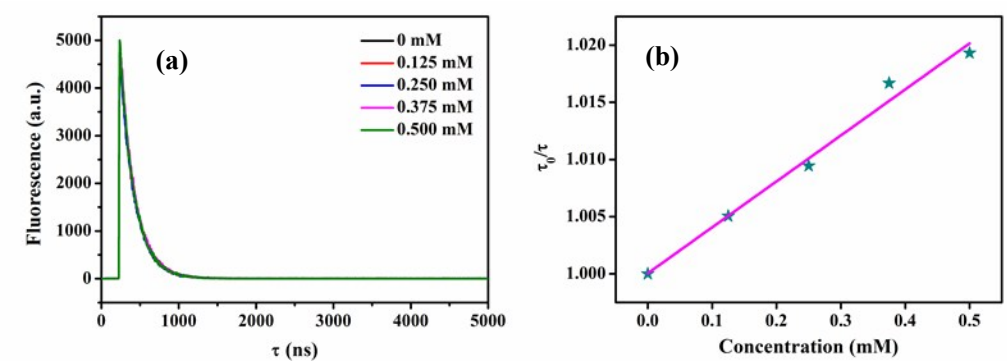


Fig. S15.4 (a) Fluorescence lifetime of 0.05 mM $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ acetonitrile/water (*v*:*v* = 4:1) solution in the presence of 0 mM (black), 0.125 mM (red), 0.250 mM (blue), 0.375 mM (magenta) and 0.5 mM (olive) of **4-Mn**. (b) τ_0/τ versus the concentration of catalyst **4-Mn**, in agreement with the Stern–Volmer equation (y = 1.4769x + 1, R^2 = 0.9997).

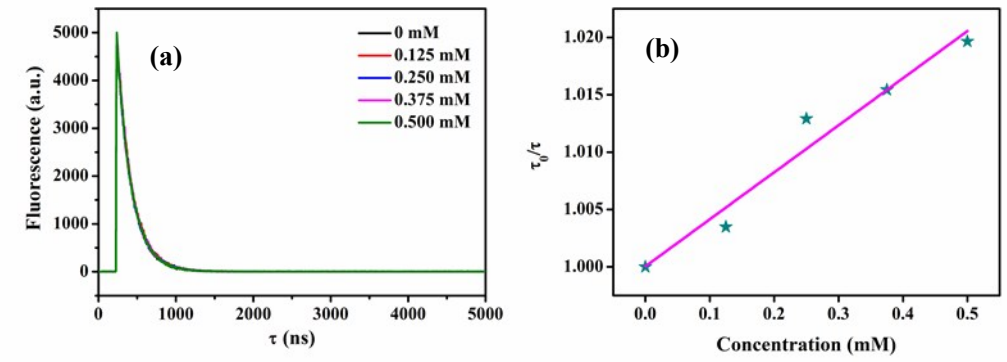


Fig. S15.5 (a) Fluorescence lifetime of 0.05 mM $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ acetonitrile/water (*v*:*v* = 4:1) solution in the presence of 0 mM (black), 0.125 mM (red), 0.250 mM (blue), 0.375 mM (magenta) and 0.5 mM (olive) of **5-Cu**. (b) τ_0/τ versus the concentration of catalyst **5-Cu**, in agreement with the Stern–Volmer equation (y = 0.43201x + 1, R^2 = 1.0028).

Computational Details

All reported structures were optimized by the density functional theory (DFT)[24] with the B3LYP functional[25] with def2-SVP basis set in the gas phase. Frequency analysis calculations of optimized structures were performed at the same level of theory (B3LYP/def2-SVP) to characterize the structures to be minima (no imaginary frequency) or transition states (one imaginary frequency). Intrinsic reaction coordinate (IRC) calculations were performed to confirm the connection between two correct minima for a transition state. Based on the (B3LYP/def2-SVP) optimized geometries, the energy results were further refined by calculating the single point energy at the B3LYP*/def2-TZVP level of theory. The B3LYP* method contains 10% HF exchange component, which is found to be appropriate to reproduce the experimental redox potential. As for the solvation effect of the mixed solvent (water/acetonitrile = 1:4), the dielectric

constant is 45.36 is set according to the reference[26] with the SMD continuum model[27] at the B3LYP* (10% HF exchange)/def2-TZVP level of theory. Considering that the translational are hindered in solution, the translational entropy is substracted in the energy. For the CO release step, the free energy of CO was corrected by its concentration (6.43×10^{-4} M), which was estimated based on its amount and solubility.[28] For the electron transfer steps, the calculated redox potential is referenced to NHE by subtracting 4.48 V.[29] All the calculations were performed with the Gaussian 09 program.[30] Localized molecular orbitals were analyzed with Multiwfn 3.6.[31] The 3D optimized structures were displayed by CYLview visualization program[32] and IQmol Molecule Viewer (http://iqmol.org/).

Table S14 Relative Free Energy in kcal·mol^{-1} for Intermediates at Different Spin States[a]

	singlet	doublet	triplet	quartet	quintuplet
$(Co^{III}(L^-)\text{-}H_2O)^{2+}$	0.0	-	15.9	-	26.3
$(Co^{II}(L^-)\text{-}H_2O)^{+}$	-	0.4	-	0.0	-
$Co^{I}(L^-)$	12.6	-	0.0	-	-
$(Co^{0}(L^-))^-$	-	0.0	-	4.5	-
$Co^{III}(L^-)(CO_2^{2-})$	0.0	-	4.0	-	23.1
$Co^{II}(L^-)(COOH^-)$	-	0.0	-	12.7	-
$[Co^{II}(L^-)\text{-}CO]^{+}$	-	0.0	-	11.3	-

[a] For each lowest energy spin state, the free energy is set as reference point 0.0 kcal/mol.

The discussion for the redox state of the active species: The energies of the intermediates at various spin states have been carefully evaluated and summarized in Table S14. In the following discussion, the reported energies and potentials are corresponding to the intermediates at the spin state with the lowest energy unless otherwise specified. First, the electron transfer steps were studied to speculate the redox state of the active species. The calculated potential for the 1-e$^-$ reduction of quartet $[Co^{II}(L^-)\text{-}H_2O]^+$ to form triplet $Co^{I}(L^-)$ accompanied with the release of one water molecule is -1.42 V (Fig. 3), which is in good agreement with the second reduction wave potential (-1.38 V) in CV of **1-Co**. Thus, we preliminarily proposed that CO_2 was activated by Co^{I} species as an enhancement of current density appeared at this wave after Ar atmosphere was replaced by CO_2. With respect to the first reduction peak, it more plausibly correspond to the process from the singlet $[Co^{III}(L^-)\text{-}H_2O]^{2+}$ to quartet $[Co^{II}(L^-)\text{-}H_2O]^+$, with a calculated potential of

-0.45 V, in good agreement with the experimental value of -0.47 V. In addition, the reduction from triplet $Co^{I}(L^{-})$ to doublet $[Co^{0}(L^{-})]^{-}$ was calculated at a highly negative potential (-2.26 V), making it almost impossible to occur in the catalytic condition.

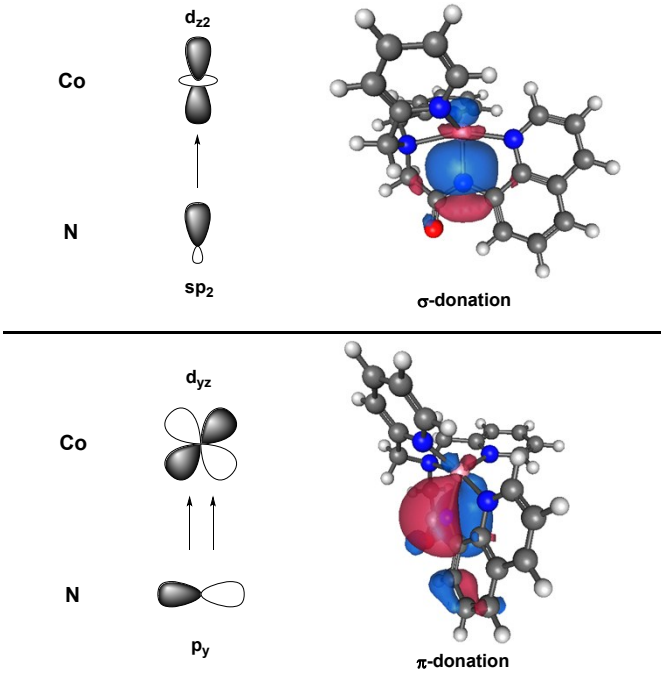


Fig. S16 σ-donation ($sp_2 \rightarrow d_{z2}$) and π-donation ($p_y \rightarrow d_{yz}$) from the amide donor to the Co center in $Co^{I}(L^{-})$.

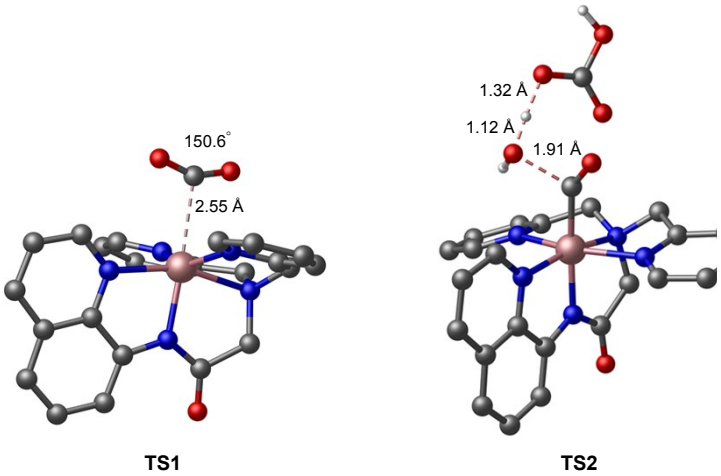


Fig. S17 Transition state structure of **TS1** and **TS2**.

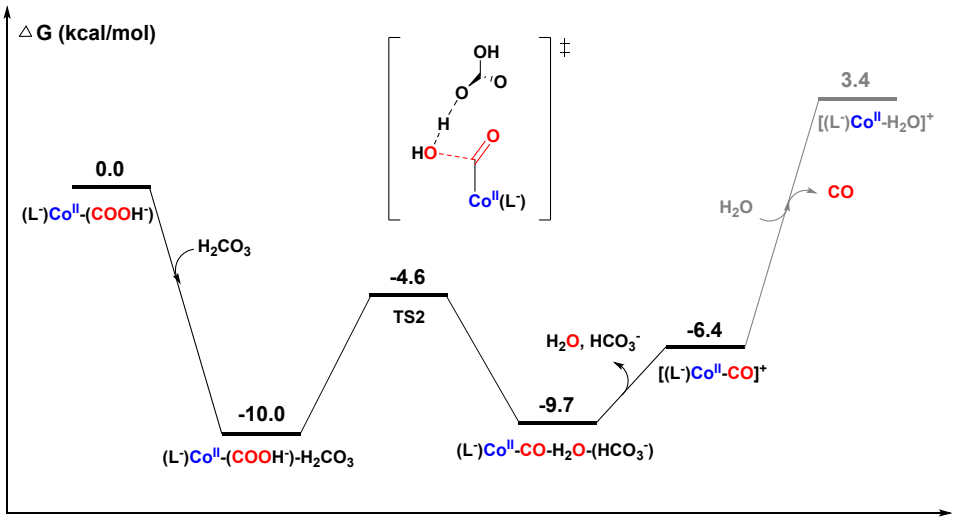


Fig. S18 The free energy profiles for the C-O cleavage process. The free energies (in kcal/mol) are calculated at the B3LYP*(10% HF exchange)/def2-TZVP/SMD//B3LYP/def2-SVP level of theory.

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The Cartesian coordinates (xyz) for all optimized structures.

$(Co^{III}(L^{-})$-$H_2O)^{2+}$(singlet)

2 1

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8 -0.388271 -0.003231 3.457229

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6 1.901243 0.020603 -2.287222

1 1.209870 0.013960 -3.132020

7 0.186492 0.001982 1.228926

6 3.292277 0.034731 -2.507285

1 3.669943 0.038877 -3.531048

7 -2.319745 -0.024270 0.332326

6 4.151700 0.042989 -1.421406

1 5.234360 0.053885 -1.572881

7 -0.726573 1.960748 -0.455885

6 3.630328 0.037234 -0.101923

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6 2.208238 0.022822 0.031640

6 1.578686 0.016029 1.306920

6 2.378501 0.023458 2.448000

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6 3.788772 0.037652 2.314468

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6 4.414781 0.044529 1.081278

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1 -2.626724 -0.906817 2.268722

1 -2.643932 0.855582 2.267072

6 -3.001527 1.211535 -0.145544

1 -3.376487 1.024568 -1.163670

1 -3.872042 1.456794 0.482991

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6 -2.338988 3.678029 0.000361

1 -3.370476 3.955268 0.227793

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1 -1.581828 5.707209 0.036661

6 -0.032052 4.251377 -0.384939

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1 1.251169 2.543644 -0.746234

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6 0.300772 -2.887666 -0.546554

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8 -1.289336 -0.013118 -2.420789

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1 -1.187167 -0.790542 -2.993269

$(Co^{III}(L^{-})$-$H_2O)^{2+}$(triplet)

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8 0.170031 0.627644 3.409826

7 1.034604 -1.080857 -1.023711

6 1.336247 -1.546776 -2.236141

1 0.730226 -1.185963 -3.069592

7 0.306153 -0.109141 1.215933

6 2.386082 -2.458510 -2.451532

1 2.590157 -2.808027 -3.465047

7 -1.698694 1.462683 0.385770

6 3.142808 -2.894034 -1.374332

1 3.964132 -3.600267 -1.521602

7 0.777065 2.048806 -0.735488

6 2.847237 -2.416830 -0.073362

7 -2.082750 -1.128162 -0.432649

6 1.768657 -1.501368 0.051731

6 1.390300 -0.961084 1.319382

6 2.108786 -1.341717 2.461207

1 1.838235 -0.935284 3.434008

6 3.181178 -2.252575 2.335788

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6 2.029494 4.496113 -0.302044

1 2.519592 5.456824 -0.127165

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6 2.084850 2.199816 -0.996889

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$(Co^{III}(L^{-})$-$H_2O)^{2+}$(quintuplet)

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6 2.307811 -0.738704 0.067024

6 1.735876 -0.203129 1.301223

6 2.566232 -0.138797 2.458752

1 2.151065 0.267059 3.379964

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1 4.509341 -0.513413 3.303841

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1 5.482012 -1.420407 1.206922

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6 -1.183506 4.246689 -0.142318

1 -2.013959 4.791244 0.312232

6 -0.040778 4.921780 -0.578229

1 0.035598 6.006129 -0.468380

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1 1.912390 4.674966 -1.503703

6 0.862292 2.806042 -1.253531

1 1.663097 2.194404 -1.678551

6 -3.315397 -0.244376 0.220774

1 -3.728981 0.018851 -0.766440

1 -4.146695 -0.162583 0.942413

6 -2.805011 -1.670864 0.157912

6 -3.603344 -2.754960 0.530242

1 -4.606534 -2.585388 0.927457

6 -3.101694 -4.051160 0.387082

1 -3.709549 -4.913580 0.670895

6 -1.809471 -4.223417 -0.114152

1 -1.374635 -5.217073 -0.236587

6 -1.070712 -3.090864 -0.450795

1 -0.050352 -3.183267 -0.831498

8 -1.193713 -0.046916 -2.688011

1 -1.199499 0.682959 -3.326592

1 -1.590802 -0.811688 -3.132395

($Co^{II}(L^{-})$-H_2O)$^{+}$(doublet)

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8 -0.334843 0.260063 3.372886

7 1.456124 -0.560309 -1.086963

6 2.003064 -0.798613 -2.273170

1 1.381961 -0.608389 -3.152759

7 0.251150 -0.055519 1.150323

6 3.322238 -1.274797 -2.424225

1 3.717480 -1.452262 -3.425889

7 -2.143402 0.766526 0.206432

6 4.086314 -1.506292 -1.296613

1 5.111530 -1.875282 -1.384784

7 0.002092 2.342799 -0.667931

6 3.540768 -1.264565 -0.008615

7 -1.514116 -1.833887 -0.587727

6 2.197143 -0.782721 0.047770

6 1.551997 -0.507241 1.296256

6 2.274262 -0.720029 2.472598

1 1.797307 -0.513902 3.428560

6 3.603899 -1.197501 2.409599

1 4.142070 -1.354761 3.347791

6 4.238304 -1.468693 1.210386

1 5.266272 -1.836221 1.186413

6 -0.572491 0.281205 2.175273

6 -1.965834 0.717612 1.695415

1 -2.693321 0.020015 2.137970

1 -2.179970 1.701955 2.139324

6 -2.373808 2.149638 -0.274779

1 -2.703688 2.083427 -1.323836

1 -3.181444 2.643636 0.292613

6 -1.102883 2.970766 -0.226053

6 -1.075403 4.297628 0.208797

1 -1.986850 4.778454 0.570520

6 0.137390 4.992479 0.176685

1 0.187946 6.030577 0.513352

6 1.280892 4.335294 -0.278739

1 2.249803 4.836821 -0.312065

6 1.164836 3.004488 -0.685718

1 2.039401 2.447041 -1.034993

6 -3.215051 -0.151182 -0.249154

1 -3.429762 0.087547 -1.303134

1 -4.148479 0.004813 0.318919

6 -2.769995 -1.596420 -0.166754

6 -3.605694 -2.622401 0.280078

1 -4.617829 -2.398712 0.624137

6 -3.120698 -3.933774 0.283468

1 -3.752315 -4.755027 0.630104

6 -1.815734 -4.173084 -0.148955

1 -1.393715 -5.179719 -0.153514

6 -1.045833 -3.087150 -0.570660

1 -0.012641 -3.226696 -0.903145

8 -1.050624 0.320144 -2.589600

1 -0.602495 0.981293 -3.138244

1 -1.138129 -0.481600 -3.126553

$(Co^{II}(L^{-})$-$H_2O)^{+}$(quartet)

1 4

27 -0.416409 0.047246 -0.576501

8 0.050573 0.746441 3.443084

7 1.433962 -0.914818 -1.022773

6 1.907284 -1.365633 -2.177238

1 1.256282 -1.243413 -3.048432

7 0.357281 0.000471 1.258463

6 3.175582 -1.966615 -2.301580

1 3.515925 -2.322908 -3.275423

7 -2.126868 1.067428 0.505789

6 3.963475 -2.086169 -1.172360

1 4.954370 -2.544543 -1.231962

7 0.060991 2.150519 -0.896749

6 3.496357 -1.612476 0.080080

7 -1.892554 -1.526067 -0.468345

6 2.191347 -1.021622 0.114726

6 1.639535 -0.518674 1.350800

6 2.430174 -0.615350 2.498972

1 2.031191 -0.230544 3.435217

6 3.717010 -1.199325 2.450267

1 4.296454 -1.256382 3.375235

6 4.253360 -1.694223 1.278153

1 5.248317 -2.143828 1.255521

6 -0.320497 0.559824 2.293059

6 -1.782354 0.923555 1.945880

1 -2.393427 0.114866 2.377860

1 -2.041097 1.835608 2.508447

6 -2.151858 2.468879 0.057611

1 -2.753783 2.521483 -0.865026

1 -2.644033 3.128233 0.794873

6 -0.776105 3.005780 -0.279535

6 -0.415174 4.332673 -0.033629

1 -1.108520 5.001491 0.480515

6 0.839638 4.784012 -0.449432

1 1.144371 5.816633 -0.263938

6 1.699340 3.892989 -1.093961

1 2.691450 4.199802 -1.429578

6 1.269413 2.580975 -1.288242

1 1.919132 1.840847 -1.763650

6 -3.343238 0.326679 0.135254

1 -3.659655 0.669950 -0.863941

1 -4.185917 0.525118 0.822823

6 -3.085121 -1.163112 0.043109

6 -4.040093 -2.113948 0.411975

1 -4.994942 -1.793713 0.834212

6 -3.753002 -3.469837 0.236687

1 -4.484366 -4.230135 0.520724

6 -2.515018 -3.836598 -0.294300

1 -2.244655 -4.883940 -0.439420

6 -1.611846 -2.828161 -0.627930

1 -0.622301 -3.067245 -1.027804

8 -1.067409 0.120185 -2.772614

1 -0.689709 0.734974 -3.417874

1 -1.416272 -0.625470 -3.281495

$Co^{I}(L^{-})$(singlet)

0 1

27 -0.519997 0.174562 -0.542910

8 0.024944 1.021883 3.395901

7 0.903641 -1.095293 -0.933169

6 1.163973 -1.689007 -2.093191

1 0.479840 -1.467925 -2.916995

7 0.273750 0.127644 1.259485

6 2.261936 -2.560740 -2.266337

1 2.428555 -3.023284 -3.241228

7 -1.828287 1.491942 0.251933

6 3.103356 -2.809708 -1.200528

1 3.960367 -3.480114 -1.309608

7 0.507678 1.786498 -1.119099

6 2.860930 -2.188659 0.055342

7 -2.017916 -1.032583 -0.651201

6 1.726788 -1.323791 0.142461

6 1.396920 -0.642769 1.368557

6 2.222857 -0.850260 2.481566

1 1.979374 -0.338641 3.411474

6 3.337714 -1.707884 2.383005

1 3.963152 -1.851817 3.268819

6 3.665746 -2.370442 1.209513

1 4.535795 -3.029080 1.157869

6 -0.319749 0.850990 2.230821

6 -1.664725 1.427685 1.738091

1 -2.439147 0.752572 2.136120

1 -1.832541 2.414210 2.199742

6 -1.491753 2.824307 -0.310039

1 -2.025087 2.901332 -1.275164

1 -1.848510 3.642895 0.338340

6 -0.023944 2.930039 -0.593234

6 0.712567 4.098771 -0.424193

1 0.234171 4.975973 0.018291

6 2.048735 4.138620 -0.835287

1 2.646261 5.044813 -0.718553

6 2.591953 2.976978 -1.398802

1 3.626623 2.947898 -1.747669

6 1.803135 1.839216 -1.514804

1 2.212022 0.924341 -1.947987

6 -3.166491 1.015208 -0.193350

1 -3.282341 1.358190 -1.237945

1 -3.985410 1.453664 0.404255

6 -3.188833 -0.479935 -0.183654

6 -4.290689 -1.241243 0.190209

1 -5.184151 -0.735761 0.565842

6 -4.251120 -2.634405 0.067590

1 -5.106900 -3.251479 0.346763

6 -3.066070 -3.204477 -0.422185

1 -2.969139 -4.285875 -0.543966

6 -1.993179 -2.391893 -0.755623

1 -1.064945 -2.827201 -1.128260

$Co^{I}(L^{-})$(triplet)

0 3

27 -0.255369 0.119693 -0.199317

8 0.969143 -1.442556 3.464215

7 1.585131 0.397455 -1.104555

6 1.871563 0.836014 -2.333385

1 1.022768 1.013727 -3.002164

7 0.925416 -0.507055 1.325447

6 3.186625 1.065111 -2.779320

1 3.355628 1.427329 -3.795844

7 -1.812640 -0.356728 1.413276

6 4.238622 0.824392 -1.916332

1 5.272449 0.992343 -2.229940

7 -1.170736 1.919759 -0.060212

6 3.981064 0.346518 -0.600213

7 -1.247112 -1.519479 -1.011097

6 2.612529 0.143762 -0.226034

6 2.275441 -0.346939 1.091441

6 3.328985 -0.617451 1.978989

1 3.080795 -0.995063 2.968451

6 4.667317 -0.409108 1.595576

1 5.458296 -0.629421 2.318362

6 5.005029 0.063310 0.337688

1 6.048390 0.220474 0.053216

6 0.400152 -1.049848 2.448409

6 -1.131392 -1.257826 2.349518

1 -1.278438 -2.295269 2.007029

1 -1.552750 -1.200788 3.370064

6 -2.089509 0.971910 1.969252

1 -3.004059 0.991809 2.594855

1 -1.240182 1.219687 2.628520

6 -2.163742 2.011891 0.878582

6 -3.122373 3.017437 0.842922

1 -3.895114 3.046647 1.615504

6 -3.083647 3.987389 -0.172244

1 -3.826948 4.785669 -0.214366

6 -2.058403 3.895332 -1.129000

1 -1.968895 4.628136 -1.934137

6 -1.136979 2.862564 -1.039106

1 -0.312638 2.782942 -1.753740

6 -2.920400 -0.950209 0.675061

1 -3.494929 -0.121426 0.218485

1 -3.632157 -1.499933 1.323812

6 -2.430599 -1.853806 -0.438315

6 -3.177288 -2.942339 -0.896328

1 -4.118149 -3.196355 -0.402123

6 -2.714159 -3.691210 -1.979934

1 -3.286027 -4.544965 -2.350438

6 -1.495525 -3.330448 -2.572909

1 -1.083352 -3.890555 -3.414398

6 -0.798486 -2.246547 -2.052256

1 0.167760 -1.943314 -2.465696

[Co^{0}(L^{-})]$^{-}$(doublet)

-1 2

27 -0.290846 0.039072 -0.230321

8 0.846614 -1.399107 3.501573

7 1.589140 0.245703 -1.123000

6 1.905814 0.634532 -2.371268

1 1.067063 0.791117 -3.057537

7 0.882562 -0.531495 1.331064

6 3.224977 0.825195 -2.801042

1 3.414243 1.144582 -3.829841

7 -1.853370 -0.230366 1.398434

6 4.271395 0.601190 -1.913418

1 5.312586 0.739982 -2.218455

7 -1.107845 1.892017 -0.217045

6 3.983264 0.175585 -0.580731

7 -1.411153 -1.389587 -1.076268

6 2.603414 0.011198 -0.222673

6 2.241153 -0.417683 1.108956

6 3.275122 -0.677629 2.030065

1 2.995857 -1.012628 3.026865

6 4.619421 -0.510980 1.662723

1 5.398384 -0.718909 2.404050

6 4.982891 -0.090968 0.387236

1 6.034791 0.035755 0.113728

6 0.313077 -1.014819 2.456888

6 -1.226680 -1.158758 2.334570

1 -1.419106 -2.183815 1.974183

1 -1.653496 -1.093986 3.355135

6 -2.002261 1.129268 1.910280

1 -2.901818 1.252277 2.551079

1 -1.122654 1.316699 2.552070

6 -1.999551 2.155502 0.799998

6 -2.770078 3.305979 0.835421

1 -3.473273 3.446152 1.662354

6 -2.633807 4.288227 -0.169685

1 -3.233847 5.200330 -0.158824

6 -1.682389 4.037336 -1.184537

1 -1.506368 4.761682 -1.984880

6 -0.963607 2.855867 -1.174852

1 -0.223401 2.643284 -1.951833

6 -3.002468 -0.748979 0.652598

1 -3.467315 0.120007 0.153004

1 -3.777474 -1.193581 1.311851

6 -2.568748 -1.743215 -0.401069

6 -3.292925 -2.881192 -0.705495

1 -4.191931 -3.104716 -0.121613

6 -2.887507 -3.735295 -1.758085

1 -3.448466 -4.636963 -2.010914

6 -1.706641 -3.368766 -2.452297

1 -1.323026 -3.981736 -3.273374

6 -1.017175 -2.229754 -2.089777

1 -0.096287 -1.942568 -2.606098

[Co^{0}(L^{-})]$^{-}$(quartet)

-1 4

27 -0.202818 0.106218 -0.225253

8 0.956817 -1.535271 3.436643

7 1.575127 0.446275 -1.071294

6 1.871420 0.946973 -2.307581

1 1.018914 1.138067 -2.968008

7 0.940550 -0.540921 1.318771

6 3.173187 1.195927 -2.732256

1 3.336854 1.599330 -3.736652

7 -1.809244 -0.403048 1.390417

6 4.251206 0.926009 -1.884185

1 5.282737 1.110877 -2.195915

7 -1.261437 1.889753 -0.084317

6 3.990587 0.387880 -0.578852

7 -1.331073 -1.394798 -1.160855

6 2.624717 0.163975 -0.207648

6 2.302875 -0.370168 1.085932

6 3.353385 -0.677912 1.977049

1 3.094829 -1.089768 2.950254

6 4.683753 -0.455856 1.602504

1 5.483524 -0.699184 2.310418

6 5.007851 0.068302 0.350705

1 6.052123 0.238617 0.069222

6 0.405761 -1.112221 2.414918

6 -1.125011 -1.327844 2.292674

1 -1.263853 -2.349890 1.902203

1 -1.552543 -1.316289 3.314704

6 -2.079890 0.909568 1.974030

1 -2.972214 0.909866 2.636249

1 -1.206308 1.151499 2.605981

6 -2.208933 1.965967 0.908854

6 -3.134936 3.003657 0.961851

1 -3.870733 3.015664 1.771810

6 -3.112592 4.022134 -0.002968

1 -3.834655 4.841070 0.023466

6 -2.119932 3.945448 -1.013666

1 -2.040037 4.711191 -1.789330

6 -1.236126 2.880679 -1.010846

1 -0.450204 2.801184 -1.769119

6 -2.926214 -0.963440 0.629192

1 -3.471880 -0.092767 0.206599

1 -3.651807 -1.508640 1.269010

6 -2.440201 -1.850013 -0.483679

6 -3.084654 -3.029094 -0.853060

1 -3.954817 -3.359615 -0.277383

6 -2.629351 -3.773263 -1.948425

1 -3.126861 -4.698801 -2.246723

6 -1.485391 -3.294176 -2.641409

1 -1.071118 -3.833203 -3.496672

6 -0.880589 -2.128223 -2.206379

1 0.016593 -1.741608 -2.701020

$Co^{III}(L^{-})(CO_2^{2-})$ (singlet)

0 1

27 -0.493481 0.111544 -0.358994

8 0.358792 0.610081 3.678048

7 1.243700 -0.761813 -0.981128

6 1.562019 -1.132023 -2.217134

1 0.764167 -0.993229 -2.954373

7 0.510793 -0.028283 1.439086

6 2.824619 -1.678510 -2.542579

1 3.026468 -1.962615 -3.577247

7 -1.945388 0.951660 0.819350

6 3.770355 -1.840542 -1.553783

1 4.755604 -2.258866 -1.779357

7 0.152693 1.963256 -0.570336

6 3.467515 -1.461820 -0.219194

7 -1.562940 -1.513819 -0.114593

6 2.167588 -0.918121 0.029534

6 1.786465 -0.512015 1.358638

6 2.724130 -0.655255 2.390422

1 2.437039 -0.339628 3.392057

6 4.001600 -1.191952 2.128055

1 4.707897 -1.290720 2.957386

6 4.381534 -1.593112 0.859498

1 5.374330 -2.007905 0.669882

6 -0.077859 0.467842 2.537230

6 -1.549416 0.830228 2.261534

1 -2.149546 0.032085 2.725750

1 -1.793567 1.756427 2.805181

6 -2.035621 2.365103 0.386641

1 -2.649912 2.382120 -0.525375

1 -2.487322 3.002324 1.165669

6 -0.681539 2.878871 -0.026157

6 -0.331297 4.227947 0.054646

1 -1.023886 4.937509 0.511814

6 0.895817 4.649624 -0.458011

1 1.186965 5.701334 -0.406555

6 1.741089 3.700530 -1.033834

1 2.710386 3.977441 -1.451894

6 1.332926 2.369056 -1.063906

1 1.966968 1.596348 -1.498815

6 -3.168974 0.165575 0.536688

1 -3.554306 0.500116 -0.438546

1 -3.945436 0.314415 1.307453

6 -2.794899 -1.288977 0.401268

6 -3.663024 -2.338741 0.699426

1 -4.645881 -2.122827 1.123272

6 -3.264280 -3.651207 0.434213

1 -3.930874 -4.488273 0.654208

6 -2.001405 -3.869022 -0.116769

1 -1.645697 -4.874833 -0.346756

6 -1.180423 -2.772528 -0.374224

1 -0.186632 -2.895868 -0.804515

6 -1.480388 0.269279 -2.157057

8 -2.375583 1.127069 -2.155837

8 -1.101205 -0.534080 -3.006451

$Co^{III}(L^{-})(CO_2^{2-})$(triplet)

0 3

27 -0.423745 0.007635 -0.395086

8 0.471155 0.778651 3.603852

7 1.493926 -0.845219 -0.978856

6 1.880538 -1.280133 -2.170438

1 1.124529 -1.218342 -2.959454

7 0.591750 0.026219 1.398005

6 3.179901 -1.781889 -2.410637

1 3.445455 -2.128689 -3.411365

7 -2.038656 0.915831 0.934365

6 4.084971 -1.816922 -1.371059

1 5.100198 -2.195264 -1.522756

7 -0.077129 2.078899 -0.735809

6 3.707210 -1.356328 -0.082515

7 -1.729195 -1.623595 -0.168822

6 2.368886 -0.871046 0.075476

6 1.907254 -0.388782 1.360193

6 2.820993 -0.401623 2.421855

1 2.486838 -0.031099 3.388418

6 4.137483 -0.881436 2.247082

1 4.812625 -0.874115 3.107657

6 4.588673 -1.354837 1.030701

1 5.609415 -1.724583 0.906688

6 -0.003368 0.549454 2.492892

6 -1.516095 0.815552 2.313175

1 -2.018143 -0.023483 2.822570

1 -1.760839 1.717480 2.900880

6 -2.190841 2.294988 0.456440

1 -2.876308 2.271071 -0.404226

1 -2.626909 2.955409 1.229810

6 -0.904330 2.900653 -0.066383

6 -0.629665 4.266784 0.051750

1 -1.311013 4.910781 0.612052

6 0.515397 4.787292 -0.552981

1 0.748314 5.851854 -0.471787

6 1.358274 3.925143 -1.256983

1 2.264471 4.286157 -1.746710

6 1.022971 2.573445 -1.316973

1 1.652661 1.853702 -1.846214

6 -3.226717 0.085323 0.699356

1 -3.681968 0.419381 -0.245386

1 -3.980505 0.184287 1.503689

6 -2.872591 -1.373089 0.497522

6 -3.717869 -2.411450 0.899053

1 -4.634334 -2.183059 1.447660

6 -3.377892 -3.729071 0.585995

1 -4.025614 -4.554533 0.891187

6 -2.198072 -3.972661 -0.120097

1 -1.893104 -4.985259 -0.390224

6 -1.401402 -2.886092 -0.476433

1 -0.468994 -3.018746 -1.030571

6 -1.441760 0.079019 -2.372493

8 -2.469289 0.725082 -2.220774

8 -0.847142 -0.530957 -3.241050

$Co^{III}(L^{-})(CO_2^{2-})$ (quintuplet)

0 5

27 -0.376845 0.000704 -0.433903

8 0.506801 0.640931 3.575351

7 1.454755 -0.898456 -1.045099

6 1.798325 -1.312090 -2.257133

1 1.027861 -1.204884 -3.028247

7 0.607950 -0.037930 1.348859

6 3.077770 -1.847096 -2.528789

1 3.319397 -2.176047 -3.541368

7 -1.961779 0.955949 0.874072

6 3.996119 -1.940011 -1.502609

1 4.994922 -2.348557 -1.682126

7 0.128672 2.173238 -0.618657

6 3.656740 -1.503030 -0.194581

7 -1.726941 -1.660602 -0.031696

6 2.340238 -0.976346 -0.004858

6 1.906054 -0.506663 1.293847

6 2.826987 -0.580676 2.345479

1 2.516433 -0.224528 3.325405

6 4.123961 -1.103390 2.142225

1 4.807075 -1.142897 2.995445

6 4.548207 -1.560192 0.909373

1 5.554591 -1.961145 0.767097

6 0.028045 0.480747 2.455873

6 -1.458180 0.861991 2.262244

1 -2.031643 0.091688 2.803368

1 -1.625971 1.803974 2.812034

6 -2.085438 2.334383 0.374773

1 -2.662250 2.281251 -0.563919

1 -2.627043 2.984235 1.088237

6 -0.760524 2.965571 0.004289

6 -0.505874 4.326614 0.202993

1 -1.237570 4.947062 0.724893

6 0.686373 4.872714 -0.276454

1 0.904974 5.933729 -0.132551

6 1.593392 4.042427 -0.937184

1 2.537349 4.425744 -1.329134

6 1.271702 2.692241 -1.078324

1 1.953915 1.996849 -1.576006

6 -3.181092 0.168584 0.635550

1 -3.576272 0.471638 -0.348247

1 -3.960966 0.357917 1.397776

6 -2.897381 -1.314273 0.534463

6 -3.832679 -2.280578 0.916704

1 -4.768810 -1.974298 1.388639

6 -3.555427 -3.628886 0.678634

1 -4.274928 -4.399866 0.964948

6 -2.345284 -3.973623 0.073400

1 -2.086137 -5.013835 -0.132387

6 -1.455768 -2.952422 -0.257941

1 -0.489341 -3.169516 -0.721107

6 -1.688089 0.270603 -2.466650

8 -2.729052 0.926521 -2.441793

8 -1.046303 -0.397763 -3.276267

$Co^{II}(L^{-})(COOH^{-})$ (doublet)

0 2

27 -0.435840 -0.033549 -0.481282

8 0.096466 -0.142880 3.607768

7 1.590584 0.269172 -1.080642

6 2.110023 0.382995 -2.295921

1 1.396559 0.356661 -3.122076

7 0.442588 0.011105 1.307232

6 3.495437 0.550508 -2.523373

1 3.863728 0.637797 -3.547829

7 -2.270234 -0.363214 0.810995

6 4.351045 0.603708 -1.444234

1 5.427911 0.734504 -1.585066

7 -1.085654 1.927548 -0.220338

6 3.834626 0.488409 -0.126193

7 -0.466314 -2.119007 -0.378829

6 2.418982 0.315467 0.010395

6 1.813055 0.182412 1.313656

6 2.659844 0.234922 2.431024

1 2.214156 0.135644 3.417450

6 4.051437 0.409015 2.278640

1 4.671813 0.443400 3.178994

6 4.645870 0.534143 1.036902

1 5.725660 0.666372 0.933399

6 -0.286006 -0.139555 2.438088

6 -1.799209 -0.324827 2.206947

1 -2.084195 -1.250273 2.735458

1 -2.298063 0.491010 2.756820

6 -3.122235 0.763456 0.440691

1 -3.560000 0.539702 -0.545014

1 -3.955136 0.924553 1.153960

6 -2.322303 2.047000 0.297323

6 -2.854194 3.296929 0.627827

1 -3.855794 3.362719 1.058881

6 -2.092934 4.444993 0.399926

1 -2.489533 5.431550 0.652170

6 -0.816672 4.307616 -0.147711

1 -0.182133 5.174696 -0.340822

6 -0.353075 3.024669 -0.440556

1 0.640355 2.861670 -0.865540

6 -2.742849 -1.675688 0.373342

1 -3.231332 -1.540930 -0.604322

1 -3.467327 -2.124864 1.081045

6 -1.595167 -2.638807 0.136542

6 -1.718906 -4.010830 0.379859

1 -2.643272 -4.402366 0.810610

6 -0.656369 -4.859749 0.067874

1 -0.733409 -5.934431 0.250709

6 0.506854 -4.309073 -0.472246

1 1.367755 -4.929832 -0.727720

6 0.556292 -2.929892 -0.673867

1 1.447452 -2.449905 -1.085912

6 -1.356107 -0.060650 -2.189083

8 -2.443614 -0.572808 -2.437379

8 -0.770375 0.632611 -3.227323

1 -1.388755 0.540521 -3.979160

$Co^{II}(L^{-})(COOH^{-})$ (quartet)

0 4

27 -0.413787 0.025054 -0.555925

8 0.348533 0.601908 3.530173

7 1.505672 -0.897353 -1.056489

6 1.912005 -1.313032 -2.246885

1 1.184606 -1.222127 -3.059874

7 0.549687 -0.028667 1.292694

6 3.207092 -1.837874 -2.460780

1 3.497354 -2.167566 -3.460521

7 -2.017543 0.947458 0.740988

6 4.077497 -1.921298 -1.393670

1 5.086795 -2.322733 -1.524420

7 0.139112 2.248675 -0.577936

6 3.672866 -1.483125 -0.104899

7 -1.720299 -1.710963 -0.011199

6 2.343873 -0.964093 0.020953

6 1.847523 -0.492388 1.297954

6 2.722203 -0.561499 2.391222

1 2.364149 -0.206961 3.355175

6 4.029207 -1.076789 2.249395

1 4.672431 -1.111044 3.133590

6 4.513284 -1.533110 1.038229

1 5.527645 -1.928221 0.942949

6 -0.075593 0.465768 2.383317

6 -1.549296 0.872724 2.141953

1 -2.154819 0.133828 2.691795

1 -1.706430 1.832419 2.663489

6 -2.149194 2.320625 0.231845

1 -2.634224 2.247170 -0.756038

1 -2.780382 2.946564 0.892284

6 -0.811508 2.995069 0.007430

6 -0.590248 4.340575 0.321796

1 -1.374631 4.923601 0.809363

6 0.640709 4.918206 0.003857

1 0.836347 5.966910 0.241398

6 1.616676 4.134290 -0.613147

1 2.594057 4.542887 -0.876964

6 1.318044 2.796624 -0.880363

1 2.052515 2.136979 -1.352617

6 -3.213712 0.138117 0.472556

1 -3.541906 0.378238 -0.552611

1 -4.043865 0.367768 1.169147

6 -2.905947 -1.343971 0.502177

6 -3.818361 -2.292424 0.977925

1 -4.771148 -1.967724 1.402003

6 -3.491529 -3.647652 0.899742

1 -4.189178 -4.406111 1.263754

6 -2.258864 -4.016209 0.358025

1 -1.959530 -5.063240 0.281120

6 -1.401522 -3.006342 -0.081717

1 -0.420759 -3.240494 -0.506531

6 -1.411423 0.181728 -2.418300

8 -2.474259 0.779966 -2.585431

8 -0.885606 -0.414466 -3.543049

1 -1.515198 -0.213423 -4.268144

[Co^{II}(L^{-})-CO]$^{+}$(doublet)

1 2

27 -0.395548 0.000194 -0.603486

8 -0.262501 0.000956 3.423370

7 1.579580 -0.001387 -1.098402

6 2.166952 -0.002095 -2.291523

1 1.520064 -0.001697 -3.172060

7 0.293492 0.000008 1.174235

6 3.568015 -0.003259 -2.452268

1 3.989591 -0.003779 -3.458761

7 -2.306679 0.001871 0.373838

6 4.374335 -0.003696 -1.331353

1 5.463287 -0.004578 -1.427215

7 -0.783855 2.164008 -0.421504

6 3.789205 -0.002984 -0.039018

7 -0.787272 -2.162871 -0.420779

6 2.361408 -0.001809 0.031172

6 1.679199 -0.001020 1.287740

6 2.446607 -0.001399 2.454793

1 1.941937 -0.000810 3.417853

6 3.858692 -0.002546 2.377922

1 4.427370 -0.002817 3.311113

6 4.531116 -0.003328 1.170671

1 5.622328 -0.004199 1.130924

6 -0.554956 0.000864 2.238900

6 -2.036055 0.001797 1.842740

1 -2.500511 -0.876732 2.316300

1 -2.499412 0.880963 2.316200

6 -2.993541 1.235559 -0.058072

1 -3.353134 1.084479 -1.090149

1 -3.882416 1.446238 0.562441

6 -2.047260 2.421109 -0.043841

6 -2.461562 3.709754 0.300982

1 -3.491837 3.890826 0.614989

6 -1.536072 4.754859 0.238437

1 -1.833902 5.771934 0.503586

6 -0.226430 4.477289 -0.156935

1 0.529655 5.262432 -0.212558

6 0.107341 3.160217 -0.475061

1 1.123057 2.891821 -0.778383

6 -2.995545 -1.230785 -0.057836

1 -3.354851 -1.079321 -1.089957

1 -3.884768 -1.439905 0.562697

6 -2.051182 -2.417872 -0.043334

6 -2.467674 -3.705820 0.301443

1 -3.498312 -3.885180 0.615237

6 -1.543901 -4.752464 0.239113

1 -1.843472 -5.769036 0.504225

6 -0.233735 -4.477070 -0.156029

1 0.521065 -5.263458 -0.211505

6 0.102270 -3.160563 -0.474155

1 1.118473 -2.893924 -0.777410

6 -0.982077 0.000295 -2.334016

8 -1.304024 0.000282 -3.425619

$[Co^{II}(L^{-})$-CO$]^{+}$(quartet)

1 4

27 -0.408712 0.029465 -0.549472

8 0.164974 0.785760 3.451497

7 1.495556 -0.863913 -1.024562

6 1.969842 -1.316856 -2.180118

1 1.307643 -1.256569 -3.049866

7 0.427005 0.026255 1.265463

6 3.262583 -1.856610 -2.322904

1 3.595599 -2.214404 -3.298580

7 -2.143967 0.943844 0.608756

6 4.081677 -1.914177 -1.211619

1 5.093140 -2.322644 -1.285723

7 -0.060162 2.183974 -0.794161

6 3.617329 -1.440850 0.040928

7 -1.796879 -1.643179 -0.307075

6 2.285012 -0.915349 0.095711

6 1.738105 -0.423413 1.335151

6 2.558282 -0.460143 2.466249

1 2.162018 -0.081233 3.405536

6 3.872226 -0.977411 2.397846

1 4.474125 -0.988607 3.309963

6 4.405324 -1.463722 1.221438

1 5.420993 -1.862836 1.180850

6 -0.241282 0.564291 2.320166

6 -1.730560 0.844332 2.034561

1 -2.278591 0.014173 2.507991

1 -2.011803 1.752530 2.591940

6 -2.285516 2.338339 0.157527

1 -2.890580 2.339246 -0.765288

1 -2.830894 2.955800 0.893497

6 -0.954432 2.976888 -0.175771

6 -0.686431 4.324457 0.073673

1 -1.424453 4.943032 0.588477

6 0.534344 4.861339 -0.342520

1 0.767116 5.912331 -0.156199

6 1.452105 4.033540 -0.991163

1 2.418964 4.409726 -1.329741

6 1.114072 2.695537 -1.190349

1 1.809601 2.005464 -1.675917

6 -3.334582 0.127593 0.316879

1 -3.731001 0.433294 -0.666744

1 -4.147234 0.293564 1.047363

6 -2.988996 -1.344811 0.243485

6 -3.865778 -2.345037 0.670292

1 -4.822888 -2.076703 1.122462

6 -3.498063 -3.683332 0.511486

1 -4.167417 -4.482098 0.839346

6 -2.261013 -3.982568 -0.062330

1 -1.930461 -5.013609 -0.198940

6 -1.438842 -2.927382 -0.454841

1 -0.455436 -3.112462 -0.895808

6 -1.037726 0.031610 -2.603772

8 -1.437496 0.032988 -3.659978