Electronic Supplementary Information for

The effects of chelating N₄ ligand coordination on Co(II)-catalysed photochemical conversion of CO₂ to CO.

Reaction mechanism and DFT calculations

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1. General experimental section

All chemicals, unless otherwise noted, were purchased from commercial sources. All solvents for synthesis, photophysical studies, and photocatalysis were of HPLC grade. The CO\textsubscript{2} gas (99.9\%) and CH\textsubscript{4} gas (>99.995\%) used in photocatalysis experiments were purchased from Hong Kong Oxygen & Acetylene Co., Ltd. and Hong Kong Specialty Gases Co. Ltd., respectively.

The nuclear magnetic resonance spectra were recorded on DPX-400 or DPX-300 Bruker FT-NMR spectrometer with chemical shift (in ppm) relative to tetramethylsilane (for CDCl\textsubscript{3}). Mass spectra (FAB) were recorded on a Finnigan MAT 95 mass spectrometer. Mass spectra (ESI-MS) were recorded on a LCQ Classic spectrometer. Elemental analysis was performed at the Institute of Chemistry of the Chinese Academy of Sciences, Beijing.

UV/Vis absorption spectra were recorded on a Hewlett-Packard 8542A diode array spectrophotometer. Steady-state emission spectra were recorded on a SPEX 1681 Fluorolog-3 spectrophotometer. The emission lifetime measurements were performed on a Quantua Ray GCR 150-10 pulsed Nd:YAG laser system. Time-solved difference absorption spectra were recorded on LP920-KS Laser Flash Photolysis Spectrometer (Edinburgh Instruments Ltd. Livingston, UK). The excitation source was 355 nm output from a Nd:YAG laser. Solutions for photophysical studies were degassed by using a high vacuum line in a two-compartment cell with five freeze-pump-thaw cycles.

X-ray diffraction data of the single crystal were collected on a Bruker X8 Proteum diffractometer. The diffraction images were interpreted and the diffraction intensities were integrated by using the program SAINT. The crystal structure was solved by direct methods employing the SHELXS-2013 program and refined by full-matrix least-squares using the SHELXL-2013 program.\textsuperscript{1}

Cyclic voltammetry (CV) and constant potential electrolysis were recorded on Princeton Applied Research Model 273A Potentiostat/Galvanostat. A three-electrode-system was used for the CV measurements; a glass carbon electrode and a platinum wire were applied as working electrode and counter electrode, respectively, for CV measurements; a carbon rod and a platinum net were applied as working electrode and counter electrode, respectively, for electrolysis. A non-aqueous Ag/AgNO\textsubscript{3} electrode or a saturated calomel electrode (SCE) was used as reference electrode. The ferrocene was used as internal standard when experiments using Ag/AgNO\textsubscript{3} electrode as reference electrode (formal potential for the Ferrocene\textsuperscript{+}/0 = 0.40 V vs.SCE).\textsuperscript{2} The electrolyte solution is 0.1 M [\textdegreeBu\textsubscript{4}N]PF\textsubscript{6} in CH\textsubscript{3}CN or DMF, which was degassed by bubbling with argon or CO\textsubscript{2} for 20 min before measurement. The working electrode was polished with a 0.05 μm alumina paste and sonicated for 15 min before use. The conductance was measured by HI8033 conductivity meter.
2. Photocatalytic CO₂ reduction, proton reduction, and hydrogenation experiments

**Photocatalytic CO₂ reduction and proton reduction:** A typical procedure for photocatalysis experiment is as follows: stock solutions with certain concentration of catalyst, photosensitizer and TEA were prepared firstly. Then certain volume of the stock solutions was added into a glass tube to give a sample with total volume of 4.0 mL. The sample tube was sealed with a rubber septum and then saturated by bubbling CO₂ gas for CO₂ reduction experiments, or argon for hydrogen production experiments for 30 min in dark. The CH₄ (500 μL) was injected as the internal standard for quantitative GC-TCD analysis. Control experiment showed that no detectable CH₄ gas was formed in the course of photocatalytic CO₂ reduction under the experimental conditions. The prepared samples were set in a photo-reactor with Blue LED lamps (λ_{max} = 460 nm) as light source. The generated gas products were characterized by GC-TCD analysis (Agilent 7890A GC System) using argon as the carrier gas with a 5 Å molecular sieve column and a thermal conductivity detector. 500 μL of gas in headspace of the tube was extracted from the sample and injected into the GC. The response factor for CO/CH₄ and H₂/CH₄ were 0.30 and 3.17, respectively, under experimental conditions, which was established by calibration with known amounts of CO, H₂ and CH₄, and determined before and after a series of measurements. The TON value was calculated based on catalyst. The selectivity for CO production is calculated according to equation: selectivity (CO) = n(CO)/n(CO + H₂).

**General procedure for photoinduced hydrogenation:** Acetophenone (0.5 mmol, 1 equiv.), cis-[Co(S,S-PDP)Cl₂] (0.005 mmol, 0.01 equiv.), Ir(ppy)₃ (0.0015 mmol, 0.003 equiv.) were dissolved in a mixed solution of TEA (1 mL), CH₃CN (2 mL) and isopropanol (2 mL) in a 15-mL reaction tube equipped with a magnetic stirring bar. The reaction tube was sealed and the solution was bubbled by N₂ for 20 min. The as-prepared sample was set in blue LED (λ_{max} = 460 nm) photo-reactor for irradiation. After reaction for certain time, a small volume of the solution was extracted for ¹H NMR analysis to determine the conversion. Finally, the solvent was removed by rotary evaporation and the product was purified by column chromatography on silica gel using CH₂Cl₂ as eluent. The purified product 1-phenylethanol, obtained as a colorless liquid, was characterized by ¹H NMR, ¹³C NMR, and HPLC analysis.

**1-Phenylethanol:** ¹H NMR (400 MHz, CDCl₃) δ 7.39–7.29 (m, 4H), 7.25 (tt, J = 4.3, 3.5 Hz, 1H), 4.84 (q, J = 6.5 Hz, 1H), 2.25 (s, 1H), 1.46 (d, J = 6.5 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 145.98, 128.63, 127.59, 125.56, 70.50, 25.28.
HPLC data of 1-phenylethanol (up, racemic; bottom, chiral)
3. Synthesis and characterization

The complexes Ir(ppy)$_3$, PDP, DMPDP, PDMBP, BQCN were synthesized according to literature procedures. The ligand TDMEA was purchased from commercial sources.

a) Ligands

**PDP**: $^1$H NMR (400 MHz, CDCl$_3$) δ 8.56–8.45 (m, 2H), 7.59 (td, $J = 7.7, 1.7$, 2H), 7.39 (d, $J = 7.8$, 2H), 7.13–7.06 (m, 2H), 4.19 (d, $J = 14.3$, 2H), 3.50 (d, $J = 14.3$, 2H), 2.99 (dt, $J = 8.9, 4.3$, 2H), 2.79 (dd, $J = 11.2, 5.1$, 2H), 2.23 (dd, $J = 17.0, 8.6$, 2H), 1.87–1.64 (m, 8H).

**DMPDP**: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.48 (t, $J = 7.7$ Hz, 2H), 7.22 (d, $J = 7.7$ Hz, 2H), 6.95 (d, $J = 7.6$ Hz, 2H), 4.15 (d, $J = 14.6$ Hz, 2H), 3.47 (d, $J = 14.6$ Hz, 2H), 3.01 (dt, $J = 8.9, 4.3$ Hz, 2H), 2.78 (d, $J = 5.8$ Hz, 2H), 2.49 (s, 6H), 2.22 (dd, $J = 16.8$, 8.4 Hz, 2H), 1.89 – 1.73 (m, 4H), 1.73 – 1.66 (m, 4H).

**PDMBP**: $^1$H NMR (300 MHz, CDCl$_3$) δ 8.49 (d, $J = 4.8$ Hz, 2H), 7.59 (td, $J = 7.6$, 1.4 Hz, 2H), 7.34 (d, $J = 7.8$ Hz, 2H), 7.16–7.04 (m, 2H), 3.61 (s, 4H), 2.50–2.38 (m, 4H), 2.23 (s, 6H), 1.81–1.66 (m, 2H).
**BQCN:** $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.81 (dd, $J = 4.0, 1.8$ Hz, 2H), 8.07 (dd, $J = 8.3, 1.8$ Hz, 2H), 7.40–7.30 (m, 4H), 7.22 (dd, $J = 8.0, 1.0$ Hz, 2H), 6.69 (d, $J = 7.7$ Hz, 2H), 4.79 (dd, $J = 5.2, 3.4$ Hz, 2H), 2.51 (s, 6H), 2.38 (d, $J = 12.9$ Hz, 2H), 1.84 (dd, $J = 6.2, 3.0$ Hz, 2H), 1.68 (d, $J = 8.2$ Hz, 2H), 1.40 (t, $J = 9.3$ Hz, 2H).

**b) Complexes**

The cobalt complexes C1-C5 were synthesized by reaction of CoCl$_2$·6H$_2$O (1.0 equiv.) with corresponding ligands (1.0 equiv.) in CH$_3$OH (10 mL) at room temperature for 1 h. By removal of two-thirds of solvent, the remaining solution was set into diethyl ether vapor for recrystallization. The product was obtained as solid crystals.

![cis-[CoII(PDP)Cl2] C1](image)

**C1:** Light purple crystals. Yield: 60%. MS (+FAB) $m/z$: 416.0 [M – Cl]$^+$. Elemental analysis Calcd. for C$_{20}$H$_{26}$Cl$_2$CoN$_4$·0.5H$_2$O: C, 52.16, H, 5.91, N, 12.17; found: C, 52.44, H, 5.85, N, 11.92.

![cis-[CoIII(DMPDP)Cl2] C2](image)

**C2:** Purple crystals. Yield: 50%. MS (+FAB) $m/z$: 443.8 [M – Cl]$^+$. Elemental analysis Calcd. for C$_{22}$H$_{30}$Cl$_2$CoN$_4$·CH$_3$OH: C, 53.92, H, 6.69, N, 10.93; found: C, 53.66, H, 6.63, N, 11.31.
C3: Dark purple crystals. Yield: 52%. MS (+FAB) m/z: 378.0 [M – Cl]+. Elemental analysis Calcd. for C$_{17}$H$_{24}$Cl$_2$CoN$_4$: C, 49.29, H, 5.84, N, 13.53; found: C, 49.28, H, 5.96, N, 13.54.

C4: Light red crystals. Yield: 69%. MS (+FAB) m/z: 490.0 [M – Cl]+. Elemental analysis Calcd. for C$_{26}$H$_{28}$Cl$_2$CoN$_4$·0.5CH$_3$CN·0.5H$_2$O: C, 58.42, H, 5.54, N, 11.36; found: C, 58.08, H, 5.48, N, 11.48.

C5: Green crystals. Yield: 70%. MS (+FAB) m/z: 324.0 [M – Cl]+. Elemental analysis Calcd. for C$_{12}$H$_{30}$Cl$_2$CoN$_4$: C, 40.01, H, 8.39, N, 15.55; found: C, 39.45, H, 8.13, N, 15.32.
4. Electrochemistry

(a) Graph showing the relationship between potential (V vs. SCE) and current (mA) at different scan rates (0.1 V/s, 0.2 V/s, 0.5 V/s, 1 V/s, 2 V/s, 5 V/s).

(b) Graph showing the relationship between potential (V vs. SCE) and current (mA) at different scan rates (0.1 V/s, 0.2 V/s, 0.5 V/s, 1 V/s, 2 V/s).
Fig. S1 cyclic voltammograms of the oxidation wave (a) and reduction wave (b) of \textit{cis}-[Co(PDP)Cl\textsubscript{2}] at different scan rates. Plot of charge accumulated (c) and current density (d) vs. time for a constant potential electrolysis in a 0.1 M [\textit{t}Bu\textsubscript{4}N]PF\textsubscript{6} acetonitrile solution containing 1.0 mM of catalyst \textit{cis}-[Co(PDP)Cl\textsubscript{2}] under CO\textsubscript{2} atmosphere; working electrode: carbon rod.
Fig. S2 Cyclic voltammograms of C2-C4 in a 0.1 M [\textsuperscript{[\textbf{n}Bu\textsubscript{4}N}\text{PF\textsubscript{6}}] acetonitrile solution under Ar (black line) or CO\textsubscript{2} (red line) atmosphere
Fig. S3 (a) Cyclic voltammograms of Ir(ppy)$_3$ in a 0.1 M [N$^\circ$Bu$_4$N]PF$_6$/DMF solution under Ar; (b) cyclic voltammograms of cis-[Co(PDP)Cl$_2$] (C) in a 0.1 M [N$^\circ$Bu$_4$N]PF$_6$/DMF solution under Ar (black line) or CO$_2$ (red line) atmosphere; scan rate: 100 mV·s$^{-1}$. 

Potential / V (vs. Ag/AgNO$_3$) 
Ir(ppy)$_3$ in DMF 
E$_{1/2}$ (Fc$^+$/Fc) = +0.09 V

Potential / V (vs. Ag/AgNO$_3$) 
Co(II)/Co(I) 
E (Fc$^+$/Fc) = 0.10 V

E$_{onset}$ = -1.91 V 
E$_{peak}$ = -2.11 V 
C$_1$ in Ar saturated DMF 
C$_1$ in CO$_2$ saturated DMF
5. UV-Vis absorption of \textit{cis}-[Co(PDP)Cl\textsubscript{2}]

\textbf{Fig. S4} UV-Vis absorption spectrum of \textit{cis}-[Co(PDP)Cl\textsubscript{2}] (4.00 \times 10^{-5} M) in DMF at room temperature.
6. Quenching experiments

![Graph](image1)

**Fig. S5** Stern-Volmer equation fitting for the emission quenching of Ir(ppy)$_3$ (4.00 $\times$ 10$^{-6}$ M) by cis-[Co(PDP)Cl$_2$] (concentration range: 8.00 $\times$ 10$^{-5}$ M - 3.20 $\times$ 10$^{-4}$ M) in degassed DMF at room temperature, excited wavelength: 400 nm.

![Graph](image2)

**Fig. S6** Emission spectra of Ir(ppy)$_3$ (P) (4.00 $\times$ 10$^{-6}$ M) in the absence (black line) and presence (red line) of TEA (0.72 M) in degassed DMF at room temperature, excited wavelength: 400 nm.
7. Transient absorption

Fig. S7 Nanosecond time-resolved difference absorption spectra of Ir(ppy)$_3$ (2.00 × 10$^{-5}$ M) in degassed DMF recorded from 0 to 4 μs after laser pulse excitation (355 nm).

Fig. S8 Decay kinetics of the difference absorption at 384 nm after excitation (355 nm) of different solution mixtures: Ir(ppy)$_3$ (2.00 × 10$^{-5}$ M) + C (1.00 × 10$^{-3}$ M) in Ar-saturated DMF (black line); Ir(ppy)$_3$ (2.00 × 10$^{-5}$ M) + C (1.00 × 10$^{-3}$ M) in CO$_2$-saturated DMF (red line); Ir(ppy)$_3$ (2.00 × 10$^{-5}$ M) + C (1.00 × 10$^{-3}$ M) + TEA (0.05 M) in Ar-saturated DMF (green line); Ir(ppy)$_3$ (2.00 × 10$^{-5}$ M) + C (1.00 × 10$^{-3}$ M) + TEA (0.25 M) in Ar-saturated DMF (blue line); (P = Ir(ppy)$_3$, C = cis-[Co(PDP)Cl$_2$]).
8. DFT calculations

Molecular structures were optimized by the M06L functional. Frequency calculations at the same level were carried out to corroborate all of the stationary points as minima (no imaginary frequency) and to compute free energies at 298.15 K. The 6-31G* Pople basis set was employed for all the atoms except for Co atom with effective core potential (ECP) type basis set LANL2DZ. The solvent effect was included by the single point calculations for all the optimized gas-phase structures with self-consistent reactions field (SCRF) based on the polarizable continuum model (PCM) in which DMF was the solvent as the experimental condition. The functional of M06 was applied in the single point calculations to compute energy; 6-311+G* basis set was applied on all the atoms except for Co atom with the Hay-Wadt relativistic effective core potentials (RECPs) LANL2TZ(f). In our simulation, the free energy of proton was taken as -11.75 eV in DMF, in which its solvation free energy was taken from computation with M062X/6-311++G(d,p). The solvation free energy for Cl in DMF was taken from experimental values. All the simulations were performed by Gaussian 09 packages.
9. Crystal structures
10. References


