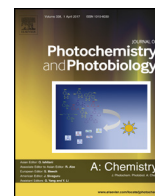




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Invited paper

Cis-[Co^{II}(MPCA)X₂] (X = Cl or Br) complexes as catalyst exhibiting different activity for visible light induced photocatalytic CO₂-to-CO conversion

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ABSTRACT

Two cobalt complexes, *cis*-[Co^{II}(MPCA)Cl₂] (**C1**) and *cis*-[Co^{II}(MPCA)Br₂] (**C2**) (MPCA = *N,N*-dimethyl-*N,N'*-bis(2-pyridinylmethyl)cyclohexane-1,2-diamine), were synthesized as catalysts for visible light induced photocatalytic CO₂ reduction. The two complexes adopt *cis*-octahedral coordination geometry with different halogen ligands at *cis*-coordination sites, which were characterized by X-ray crystal analysis. The two cobalt catalysts exhibited different activity on catalysing CO₂-to-CO conversion in the presence of Ir(ppy)₃ as photosensitizer and triethylamine as sacrificial electron donor in DMF under visible light irradiation. The rate of CO production of **C2**-system was faster than that of **C1**-system in the initial stage of irradiation. However, the better stability of **C1**-system than that of **C2**-system leading a total TON_{CO} of 470 from **C1**-system compared with of 403 from **C2**-system were obtained after 48 h of irradiation. Mechanism studies revealed that the photoinduced electron transfer from Ir(ppy)₃^{*} to cobalt complex, **C1** or **C2**, operates to generate active Co^I species for CO₂ binding. The **C2**-system possesses larger rate constant and driven force of the photoinduced electron transfer process than those of in **C1**-system.

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1. Introduction

The construction of artificial photosynthetic system for conversion of carbon dioxide (CO₂) into fuels or their precursors, such as carbon monoxide (CO), is an area of blooming interest recently [1–5]. One of key challenges for efficient reduction of molecule CO₂ under either photocatalytic or electrocatalytic condition is developing of novel catalysts with high activity and selectivity. Metal complexes, such as Re(I), Ru(II), Ir(III) complexes, as a main class of catalysts had long been explored to mediate CO₂ reduction in photocatalytic and/or electrocatalytic systems [6–11]. However, the reports of photocatalytic CO₂ reduction by using of earth abundant metal (Fe, Co, Ni) complex as catalyst are still rare [10,12]. Recent studies involving cobalt [13–16], iron [17–25], or nickel complexes [26–30], such as a Ni^{II}-carbene-amine complex [26], a hydroxyl functionalized Fe^{III}-porphyrin [17], and a Co^{II}-

quaterpyridine complex [21], as catalysts for photocatalytic CO₂-to-CO conversion demonstrated the promising results of high turnover number (TON) and selectivity.

Of particular interest on cobalt complexes, we noted that Co^{II}-complexes with trigonal bipyramid or octahedral geometry had been described recently to efficiently catalyse CO₂-to-CO conversion under photocatalytic conditions [13,16]. Especially, a series of cobalt complexes adopting octahedral coordination geometry with two *cis*-chloride ligands were newly reported by Che et al. to reductively catalyse CO₂-to-CO conversion with high faraday efficiency or high turnover number in either electrocatalytic or photocatalytic systems [16]. The one with highest activity among this series is a *cis*-[Co(PDP)Cl₂] complex, where the PDP ligand is a tetradentate N atom (N₄) ligand with a bipyrolidine as a framework and two pyridinylmethyl groups as pincers. Mechanism studies on DFT calculations revealed that the chloride ligand staying at *cis*-position in the *cis*-[Co(PDP)Cl₂] complex plays an important role of assisting bound CO₂ in attracting protons. The results demonstrated the advantage of *cis*-coordination geometry

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as well as the importance of auxiliary ligand at *cis*-coordination site for the conversion of CO₂ molecule at cobalt center.

Herein, we reported two cobalt complexes *cis*-[Co^{II}(MPCA)Cl₂] (**C1**) and *cis*-[Co^{II}(MPCA)Br₂] (**C2**) (Scheme 1). The two complexes are supported by MPCA ligand (MPCA = *N,N'*-dimethyl-*N,N'*-bis(2-pyridinylmethyl)cyclohexane-1,2-diamine), which is an analogous structure of PDP ligand. The two complexes adopting *cis*-octahedral geometry contain different halogen ligands at *cis*-positions in the solid state. We utilized these two cobalt complexes as catalyst for photocatalytic CO₂ reduction in a typical homogeneous photocatalytic CO₂ reduction system of containing Ir(ppy)₃ as a photosensitizer and triethylamine (TEA) as a sacrificial electron donor. The two complexes showed high catalytic activity and selectivity for CO₂-to-CO conversion under above photochemical conditions; however, two complexes exhibiting of different initial rate and stability for CO production were also observed.

2. Materials and methods

2.1. Reagents and instruments

All chemicals, including gases, CO₂ (99.999%) and CH₄ (>99.99%), were purchased from commercial sources. All solvents for synthesis, photophysical studies, and photocatalysis were HPLC grade. 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 CDCl₃). Mass spectra (FAB) were recorded on a Finnigan MAT 95 mass 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 spectrophotometer (Specord 50, Analytic Jena, Germany). The emission spectra were recorded on Edinburgh spectrometer FLS-980, equipped with MCP-PMT and NIR-PMT detectors. The emission lifetime measurements were performed on a Quantua Ray GCR 150-10 pulsed Nd:YAG laser system. The excitation source was 355 nm output from a Nd:YAG laser. Solutions for photophysical studies were degassed by nitrogen. 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. The cyclic voltammetry (CV) were recorded on CHI 760E electrochemical

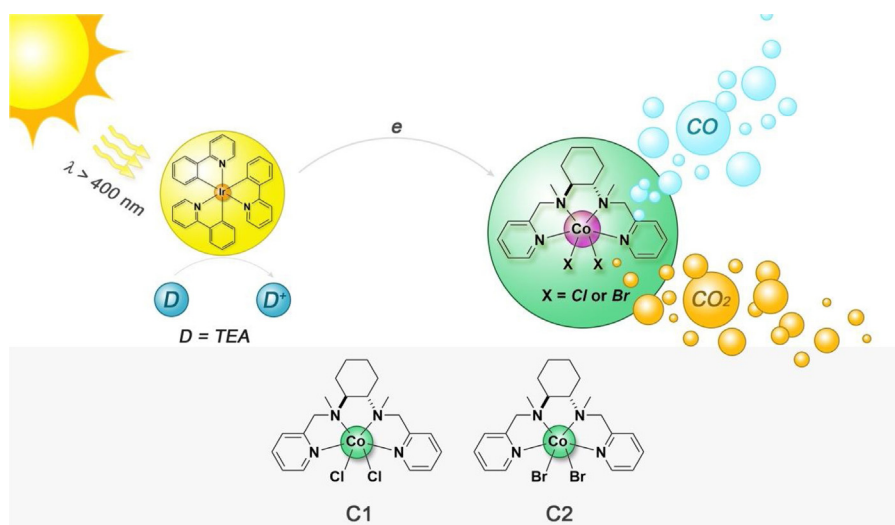
workstation (CH Instruments, China). A three-electrode-system, a glass carbon electrode as working electrode, a non-aqueous Ag/AgNO₃ electrode as reference, and a Pt wire as counter electrode, was used for the CV measurements; The ferrocene (Fc) was used as internal standard. The electrolyte solution is 0.1 M *n*-Bu₄N⁺PF₆⁻ in DMF, which was degassed by bubbling with N₂ or CO₂ for 20 min before measurement. The working electrode was polished with a 0.05 μm alumina paste and sonicated for 15 min before use.

2.2. Synthesis

The ligand MPCA was synthesized according to literature procedures[31]. The ¹H NMR data of MPCA ligand as follows: ¹H NMR (400 MHz, CDCl₃) δ 8.49 (d, *J* = 3.6 Hz, 2H), 7.58 (d, *J* = 11.9 Hz, 4H), 7.11 (s, 2H), 3.85 (m, 4H), 2.65 (d, *J* = 8.2 Hz, 2H), 2.28 (s, 6H), 2.00 (s, 2H), 1.75 (s, 2H), 1.26 (d, *J* = 7.4 Hz, 2H), 1.17 (d, *J* = 9.6 Hz, 2H). The complexes **C1** were synthesized by stirring CoCl₂·6H₂O and MPCA ligand with a mole ratio of 1:1 in methanol at room temperature for one hour. A large volume of Et₂O was added into the dark brown CH₃OH solution to obtain pale purple participates. These participates were collected for recrystallization. The dark purple crystals of **C1** were obtained by recrystallization in CH₃OH/Et₂O system (yield: 68%). **C1**: MS (+FAB) *m/z*: 418.0 [M – Cl]⁺. Elemental analysis Calcd. for C₂₀H₂₈Cl₂CoN₄·0.5H₂O: C, 51.94, H, 6.32, N, 12.12; found: C, 51.62, H, 6.42, N, 12.33. The complex **C2** were synthesized by the same procedures except using CoBr₂ as a cobalt source. The obtained crystal of **C2** is dark purple solid with a yield of 50%. **C2**: MS (+FAB) *m/z*: 461.9 [M – Br]⁺. Elemental analysis Calcd. for C₂₀H₂₈Br₂CoN₄: C, 44.22, H, 5.20, N, 10.31; found: C, 43.77, H, 5.51, N, 9.94.

2.3. Photocatalytic CO₂ reduction

A typical procedure for photocatalysis experiments is as follows: stock solutions with certain concentration of catalyst and photosensitizer were prepared firstly. Then certain volume of the stock solutions and TEA was added into a glass tube to give a sample with total volume of 5.0 mL. The sample tube was sealed with a rubber septum and then saturated by bubbling CO₂ gas for 20 min in dark. The CH₄ (500 μL) was injected as the internal standard for quantitative GC 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



Scheme 1. The chemical structures of **C1** and **C2**, and the photocatalytic system for CO₂-to-CO conversion.

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