Enhancement of electrocatalytic abilities for reducing carbon dioxide: Functionalization with a redox-active ligand-coordinated metal complex

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Enhancement of electrocatalytic abilities for reducing carbon dioxide: Functionalization with a redox-active ligand-coordinated metal complex


A binary system consisting of a ditopic planar pseudo-pincer ligand (qlca = quinoline-2-carbaldehyde (pyridine-2-carbonyl) hydrazone) coordinated to two metal centres affording ([Ru(bpy)₂(µ-qlca)]NiCl₂·4H₂O·CH₃OH) (2) (bpy = 2,2'-bipyridine) is reported. The Ni⁺⁺ moiety acts as the electrocatalytically active site for CO₂ reduction to CO. The turnover frequency (TOF) increased from 0.83 s⁻¹ for [Ni(qlca)Cl] (3) to 120 s⁻¹ for 2, and the overpotential is 350 mV less than that for 3 due to the electronic influence of the (Ru(bpy)₂)⁺⁺ moiety on the catalytic active site.

Conversion of CO₂ to low-carbon fuels is an excellent way to meet the increasing demand for energy while lowering the impact of CO₂, a primary greenhouse gas, on the environment. Although several approaches have been used to develop efficient and selective catalysts for CO₂ reduction, challenges remain. A key challenge is the development of CO₂-selective homogeneous electrocatalysts, which are highly active and selective for the specific catalytic process at low overpotential. State-of-the-art CO₂ reduction electrocatalysts, such as Mn, Co and Fe complexes, have high catalytic performance at very low overpotentials.

Another way to improve electrocatalytic abilities is to utilize redox-active ligands attached redox-active metal complexes to electrocatalysts to improve their electrocatalytic abilities. Since ruthenium polypyridyl moieties, like {Ru(bpy)₂}⁺⁺, have rich redox properties and have a cationic metal ion, we have recently started exploring their use to enhance catalytic abilities. In this work, we used a ditopic planar redox-active pseudo-pincer ligand, quinolone-2-carbaldehyde (pyridine-2-carbonyl) hydrazone (qlca), to tether a redox-active metal complex, {Ru(bpy)₂(qlca)}⁺⁺, to electrocatalyst moiety, which allows for more electron density near the active site. Since the redox-active metal complex and electrocatalytic centre are tethered in close proximity to each other, we believed that the electrocatalytic ability towards the conversion of CO₂ to CO would be improved while maintaining the selectivity and decreasing the overpotential.

The synthesis and structural diagrams of the complexes are shown in Scheme 1, and detailed synthetic procedures are provided in the Electronic Supplementary Information (ESI). The bridging ligand qlca was prepared following a previously reported procedure. [Ru(bpy)₂(qlca)]Cl (1) was synthesized.
by mixing cis-[Ru(bpy)₂Cl₂] and qlca in ethanolic solution (see ESI).

\[
\text{[Ru(bpy)₂Cl₂]} + \text{qlca} \xrightarrow{\text{EtOH, reflux, 12 h}} \text{[Ru(bpy)₂(qlca)]^+} (1) \ \text{yield: 80%}
\]

\[
\text{[Ru(bpy)₂(qlca)]^+} + \text{NiCl₂-H₂O} \xrightarrow{\text{EtOH, 1 drop Et₃N, stir, room temp, 1 h}} \text{[Ru(bpy)₂(qlca)NiCl₂]} (2) \ \text{yield: 75%}
\]

Scheme 1. Synthesis and structural diagrams of [Ru(bpy)₂(qlca)]⁺ (1), [Ru(bpy)₂(u-qlca)NiCl₂]⁺ (2) and [Ni(qlca)Cl₂]⁻ (3).

3 was obtained from the reaction of NiCl₂·H₂O and qlca in ethanol in the presence of trimethylamine. 2 was obtained by reacting NiCl₂·H₂O and 1 in an ethanolic solution. Deep-red plate-like single crystals of 2 were obtained after 3–4 days.

Fig. 1 ORTEP diagram of 2 at 50% probability. Hydrogen atoms and solvent molecules are omitted for clarity. Selected bond distances (Å): N1-N5 = 2.07(2); N1-N6 = 2.01(2); N1-C11 = 2.36(2); N1-C12 = 2.33(2); N6-N7 = 1.39(2); Ru1-N7 = 2.04(2); Ru1-O1 = 2.07(1); Ru1-N1 = 2.11(2); Ru1-N2 = 2.09(1); Ru1-N3 = 2.09(2); Ru1-N4 = 2.03(2); C26-O1 = 1.28(2). Selected bond angles (°): C11-N1-C12 = 147.1(2); N5-N1-C11 = 89.1(5); N5-N1-C12 = 92.0(5); N5-N1-N6 = 80.5(5); N5-N1-N8 = 174.0(6); N1-Ru1-N7 = 172.6(6); O1-Ru1-N7 = 79.3(3).

An ORTEP diagram of 2 is shown in Fig. 1, and the crystal data are summarized in Table S1. 2 crystallizes in the monoclinic space group P2₁. The asymmetric unit is composed of two bpy ligands coordinated to a RuII ion, one NiI ion coordinated by two Cl⁻ ions, one qlca ligand bridging the RuII and NiI ions and a Cl⁻ ion as a counter ion. Similar to the structure reported by A. Mori et al., the hydrazone group of the qlca ligand is deprotonated.25 Atoms N8, N6 and N5 of the qlca ligand coordinate to the NiI ion in a tridentate mode. The RuII ion in the [Ru(bpy)₂]⁺ moiety adopts an octahedral geometry and is coordinated by atoms N7 and O1 of qlca in a bidentate mode. The O1–C26, C26–N6 and N6–N7, N7–C27 bond lengths were determined to be 1.28(3), 1.36(3), 1.38(3), and 1.31(3) Å, respectively, suggesting that the negative charge of the ligand is delocalized in this region.25,34 In ESI mass spectra (Fig. S2), the molecular ion peak was observed at 817 2m/z, which corresponds to [([Ru(bpy)₂]µ-qlca)NiCl₂]⁺. There are methanol and four water molecules per asymmetric unit at 93 K. Elemental analysis of desolvated 2 was consistent with the calculated value for [([Ru(bpy)₂]µ-qlca)NiCl₂]Cl.

Electrochemical properties of 2 and 3 were investigated by using cyclic voltammetry (see ESI for details). Cyclic voltammograms (CVs) of 3 were acquired in 5:95 (v/v) mixture of H₂O and CH₂CN containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) saturated with N₂ and CO₂ are shown in Fig. 2a. The broad wave at −0.40 V and wave at −0.72 V vs. NHE were assigned to be due to the first and second reduction of the qlca ligand, respectively. The waves at −1.30 V and −1.61 V vs. NHE were assigned to nickel I/I couples, respectively. Under CO₂, the catalytic current slightly increased, indicating weak electrocatalysis.

For 2 (Fig. 2b), in dry CH₂CN solution, the waves at −0.18 V (under CO₂ same wave appeared for 3) and −0.62 V vs. NHE were assigned to the first and second reduction of the qlca ligand, and those at −0.45 and −0.95 V vs. NHE were assigned to first and second reduction of bpy ligands, respectively. The waves at −1.20 V and −1.42 V vs. NHE assigned to the NiI and NiII couples, respectively.
The waves for the Ni$^{II}$ and Ni$^{III}$ couples were at less negative potentials than those for 3 (Fig. 2d) because of cationic effects of the Ru$^{3+}$ center. A similar behavior has been observed when Ca$^{2+}$ or Na$^+$ is added to other electrocatalytic systems. The current was enhanced, indicating the reduction of CO$_2$, and the enhancement was much higher than that using 3, showing the electronic influence of (Ru(bpy)$_3$)$_2^{2+}$ moiety on the electrocatalytic center. The CVs of 2 in 5:95 (v/v) mixture of H$_2$O and CH$_3$CN (v/v) and found that the reduction wave for the Ni$^{II}$ couple decreased at ~1.17 V and the Ni$^{III}$ couple at ~1.40 V vs. NHE (Fig. 2c). Under CO$_2$, the increase in the catalytic current was larger than that using 3, and the catalytic potential was shifted positively. Although the overall negative charge of 3 causes the Ni$^{III}$ reduction potential to be more negative and makes a direct comparison of the CVs of 2 and 3 difficult, it is clear that attaching a cationic redox-active (Ru(bpy)$_3$)$_2^{2+}$ moiety causes a positive shift in the Ni$^{III}$ potential as well as the catalytic potential (Fig. 2d), reducing the overpotential needed to reduce CO$_2$.

Control potential electrolysis (CPE) experiments were performed to determine the catalytic abilities of 2 and 3 for CO$_2$ reduction. CPE was performed for 30 min at potentials necessary for electrocatalytic activity. Samples of the headspace were obtained by using a gas-tight syringe during electrocatalysis and analyzed by using gas chromatography-mass spectrometry (GC-mass). In the gas phase, the main product in both cases was CO. The Faradaic efficiencies for CO were determined to be 61% for 3 and 82% for 2 in 5:95 (v/v) H$_2$O/CH$_3$CN. The turnover frequencies (TOFs) were determined from CPE data at ~1.55 V for 3 and ~1.20 V vs. NHE for 2 to be 0.83 and 120 s$^{-1}$, respectively, by using Eq. 1, which McCrorry et al. modified from equations introduced by Savéant and coworkers.

$$\text{TOF} = \frac{(i_{el})^2 (1 + \exp \left( \frac{F}{RT} (E_{app} - E_{1/2}) \right))}{F^2 A^2 D [\text{cat}]^2} \quad \text{Eq. 1}$$

where $i_{el}$ is the average current of CPE for CO generation (A), $F$ is Faraday’s constant (96500 C/mol$^e$), $R$ is the universal gas constant (8.31 JK$^{-1}$mol$^{-1}$), $T$ is the temperature (298 K), $E_{app}$ is the applied potential during CPE, $E_{1/2}$ is the standard redox potential of the catalyst, $A$ is the surface area of working electrode (0.196 cm$^2$), $D$ is the diffusion coefficient for catalyst and [cat] is the concentration of catalyst in solution. The overpotentials using 2 and 3 are 480 and 830 mV. In other words, (Ru(bpy)$_3$)$_2^{2+}$ lowers catalytic potential.

In summary, we designed a new binary system consisting of a redox-active metal complex (Ru(bpy)$_3$)$_2^{2+}$ and a metal centre with an electrocatalytic active site (Ni$^{II}$) connected via a ditopic planar redox-active pseudo pincer-type ligand. The catalytic abilities of 2 were improved due to the electronic influence of redox-active (Ru(bpy)$_3$)$_2^{2+}$ moiety. TOF increased from 0.83 s$^{-1}$ for 3 to 120 s$^{-1}$ for 2. The overpotential for 2 is 350 mV less then 3. These results show the advantages of tethering a redox-active moiety to an electrocatalyst, and we are currently applying this approach to other electrocatalytic systems.

**Conflicts of interest**

There are no conflicts to declare.

**Acknowledgements**

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**References**

Attaching a redox-active metal complex to a CO$_2$ reduction electrocatalyst improves the overpotential and turnover frequency towards the reduction of CO$_2$ to CO.