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# Ligand-assisted electrochemical CO<sub>2</sub> reduction by Ru-polypyridyl complexes

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Dedication ((optional))

**Abstract:** The introduction of a simple triazole moiety on a terpyridine ligand in the complex  $[Ru(tpy)(bpy)(Cl)]^{+}$  ([1]<sup>+</sup>; tpy = 2,2':6',2''-terpyridine; bpy = 2,2'-bipyridine) gives rise to a suitable electrocatalyst for the reduction of CO<sub>2</sub> to CO. The triazole group in  $[Ru(tpyaz)(bpy)(Cl)]^{+}$  ([2]<sup>+</sup>; tpyaz = 4'-(4-(t-butylphenyl)-1H-1,2,3-triazol-4-yl)-2,2':6',2''-terpyridine) enables the complex [2]<sup>+</sup> to bind with CO<sub>2</sub> even at the one-electron reduced state of the complex. Further 2<sup>nd</sup>-electron addition after CO<sub>2</sub>-coordination to the catalyst facilitates efficient CO<sub>2</sub> reduction, based on cyclic voltammetry analysis.

#### Introduction

Nature has developed effective catalysts for CO<sub>2</sub> reduction in the light-independent reactions of photosynthesis. The efficient reduction and fixation of CO2, a greenhouse gas, would significantly decrease its associated environmental risks and offer a sustainable route for the production of carbon-based feedstocks. Therefore, it is highly desirable to develop new, simpler CO<sub>2</sub> reduction catalysts that use solar or electrical energy to produce energy-dense products, e.g. formic acid (HCOOH), carbon monoxide (CO), formaldehyde (HCHO) and methanol (CH<sub>3</sub>OH). Currently, many encouraging results have been reported for photochemical<sup>[1]</sup> and electrochemical<sup>[2,3]</sup> CO<sub>2</sub> reductions that require two electrons to generate CO or HCOOH. Among various metal complexes, Ru-polypyridyl complexes have received much attention,<sup>[2a,d,e,3,4b]</sup> due to their efficiency and stability. Moreover, Ru-polypyridyl complexes have significantly lower overpotentials associated with CO<sub>2</sub> reduction compared to those of other active metal complexes.<sup>[2a,3]</sup> In this regard, we recently developed new Ru<sup>II</sup>-NAD (NAD = nicotinamide adenine dinucleotide) polypyridyl  $complexes^{[4a]}$  and explored their electrocatalytic activity for CO2 to

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Supporting information for this article is given via a link at the end of the document: CVs of complexes [1]\* and [2]\* in presence of mixed  $H_2O/CH_3CN$  solutions, characterization data for tpyaz-ligand, complexes [2]\* and [3]<sup>2+</sup>, 1H, <sup>13</sup>C NMR spectra of corresponding ligand and complexes. This Supporting Information file is available free of charge on the Willey publication website at DOI.

HCOOH reduction in MeCN/H<sub>2</sub>O mixed solvents.<sup>[4b]</sup> Herein, we have synthesized two new Ru<sup>II</sup>-polypyridyl complexes, [Ru(tpyaz)(bpy)(Cl)][PF<sub>6</sub>], [2][PF<sub>6</sub>] and [Ru(tpyaz)(tpy)][PF<sub>6</sub>]<sub>2</sub>, [3][PF<sub>6</sub>]<sub>2</sub> (Figure 1). We tested their CO<sub>2</sub> reduction abilities by cyclic voltammetry under different reaction conditions and compared the results to previously reported complexes [Ru(tpy)(bpy)(Cl)][PF<sub>6</sub>], [1][PF<sub>6</sub>], and [Ru(tpy)<sub>2</sub>][PF<sub>6</sub>]<sub>2</sub>, [4][PF<sub>6</sub>]<sub>2</sub>. Controlled-potential electrolysis at -1.55 V (vs. FeCp<sub>2</sub><sup>+/0</sup> using ferrocene as internal standard) under a CO<sub>2</sub> atmosphere produced CO as the main product using [1]<sup>+</sup> and [2]<sup>+</sup>, with [2]<sup>+</sup> showing a higher CO/HCOOH ratio. In contrast, [3]<sup>2+</sup> and [4]<sup>2+</sup> generated H<sub>2</sub> as the main reduction product under the same conditions.



Figure 1: Chemical structures of  $[1][PF_6]$ ,  $[2][PF_6]$ ,  $[3][PF_6]_2$  and  $[4][PF_6]_2$ ;  $[PF_6]$  hexafluorophosphate as counter ion.

#### **Results and Discussion**

Ligand tpyaz was synthesized based on a previously reported method with slight modifications (Scheme S1, see SI for full synthetic details).<sup>[6]</sup> Complexes [1][PF<sub>6</sub>]<sup>[6]</sup> and [4][PF<sub>6</sub>]<sup>[7]</sup> were synthesized according to literature procedures.

# Synthesis and crystal structures of complexes $\mbox{[2]}[\mbox{PF}_6]$ and $\mbox{[3]}[\mbox{PF}_6]_2$

Complexes [2][PF<sub>6</sub>] and [3][PF<sub>6</sub>]<sub>2</sub> are both readily available via a two-step synthesis starting from RuCl<sub>3</sub>·xH<sub>2</sub>O (Scheme 1), respectively. As such, [RuCl<sub>3</sub>(tpyaz)] was obtained by reacting RuCl<sub>3</sub>·xH<sub>2</sub>O first with tpyaz (75% yield), followed by bpy in the presence of triethylamine to give [2]<sup>+</sup> as a reddish-brown solid, which was isolated as the hexafluorophosphate salt in 82% yield (Scheme 1a). Alternatively, [RuCl<sub>3</sub>(tpyaz)] was treated with tpy in presence of triethylamine to give [3]<sup>2+</sup> as a deep red solid, which was isolated as hexafluorophosphate salt in 85% yield (Scheme 1b). Fig. 2 shows the molecular structures of [2][PF<sub>6</sub>] and [3][PF<sub>6</sub>]<sub>2</sub> determined by X-ray crystallography (Table S1).<sup>[8]</sup> Both [2][PF<sub>6</sub>] and [3][PF<sub>6</sub>]<sub>2</sub> were recrystallized from MeCN/Et<sub>2</sub>O. The ruthenium

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ion in complex [2][PF<sub>6</sub>] shows an octahedral configuration formed by five nitrogen atoms (three of tpyaz and two of bpy ligand) and one Cl ligand. The complex [3][PF<sub>6</sub>]<sub>2</sub> also displays an octahedral configuration formed by six nitrogen atoms (three of tpyaz and three of tpy ligand). The dihedral angles between the central pyridine and triazole in [2][PF<sub>6</sub>] (Figure 2a) and [3][PF<sub>6</sub>]<sub>2</sub> (Figure 2b) (12.12° for [2]<sup>+</sup> and 3.56° for [3]<sup>2+</sup>) and between triazole and the next benzene ring (11.18° for [2]<sup>+</sup> and 15.32° for [3]<sup>2+</sup>) indicate that both complexes are almost coplanar.



The Ru-N bond lengths in both complexes were comparable to those in  $[4]^{2+,[9]}$  The <sup>1</sup>H NMR spectrum of  $[2][PF_6]$  in CD<sub>3</sub>CN displayed eleven signals integrated to 23 protons in the aromatic region, while that of  $[3][PF_6]_2$  revealed 11 signals integrated to 26 protons also in the aromatic region. The <sup>1</sup>H signals of the tpyaz-

ligand in [2][PF<sub>6</sub>] and [3][PF<sub>6</sub>]<sub>2</sub> were slightly downfield shifted compared to the pure tpyaz ligand.<sup>[5]</sup> This is due to the complexation of the tpyaz ligand with Ru both in [2][PF<sub>6</sub>] and [3][PF<sub>6</sub>]<sub>2</sub>.



Figure 2: Crystal structure of complexes (a) [Ru(tpyaz)(bpy)(Cl)]+ [2]+ and (b) [Ru(tpyaz)(tpy)]<sup>2+</sup> [3]<sup>2+</sup> with 50% thermal ellipsoids. The counter anions, the solvent molecules and the hydrogen atoms are omitted for clarity.

## Electrochemical behaviour of complexes $[1]^{+}-[4]^{2+}$ under inert and CO<sub>2</sub> atmosphere.

The cyclic voltammogram (CV) of [1]<sup>+</sup> in MeCN under an argon atmosphere (Figure 3, black) showed a reversible reduction couple at  $E_{1/2}$  = -1.63 and an irreversible redox wave at  $E_{pc}$  = -1.87 V. These redox waves are attributed to redox reactions localized on tpy and bpy, respectively, in accordance to a previous report.<sup>[3d]</sup> Likewise, the CV of [2]<sup>+</sup> in CH<sub>3</sub>CN under inert atmosphere (Figure 4, black) showed a reversible reduction couple at  $E_{1/2} = -1.57$  V and an irreversible redox at  $E_{pc} = -1.86$  V. They are assignable to redox reactions localized on the tpy moiety of tpyaz and bpy, respectively, similar to [1]<sup>+</sup> in CH<sub>3</sub>CN (*cf.* Figure 3, black). Introduction of CO<sub>2</sub> (solvent saturation for 20 min) to the solution of [1]<sup>+</sup> resulted in the appearance of catalytic current near the second redox wave (threshold potentials of -1.76 V, *cf.* Figure 3, red). Interestingly, complex [2]<sup>+</sup> under similar conditions showed significant two-step current enhancement near both first and second redox waves (threshold potentials of -1.55 V and -

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1.78 V, respectively, *cf.* Figure 4, red). This result indicates that the triazole moiety of tpyaz may have direct interaction with  $CO_2$  causing increase of current near the first redox wave.



Figure 3. Cyclic voltammograms of [1]<sup>+</sup> under Ar (black) and CO<sub>2</sub> (red) at a scan rate  $\nu$  = 100 mV s<sup>-1</sup>. Conditions: glassy carbon electrode, 1 mM [1]<sup>+</sup>, 0.1 M [Bu<sub>4</sub>N][PF<sub>6</sub>], in CH<sub>3</sub>CN.



Figure 4. Cyclic voltammograms of [2]<sup>+</sup> under Ar (black) and CO<sub>2</sub> (red) at a scan rate  $\nu = 100$  mV s<sup>-1</sup>. Conditions: glassy carbon electrode, 1 mM [2]<sup>+</sup>, 0.1 M [Bu<sub>4</sub>N][PF<sub>6</sub>], in CH<sub>3</sub>CN.

Inspired by these observations, we recorded CVs of  $[3]^{2+}$  in CH<sub>3</sub>CN under both an argon and CO<sub>2</sub> atmosphere and compared the results with those of the reported complex  $[4]^{2+}$ . The CV of  $[3]^{2+}$  in CH<sub>3</sub>CN under an argon atmosphere (Figure 5, black) showed two reversible reduction couples at  $E_{1/2} = -1.50$  and -1.77 V, which are attributed to ligand redox reactions localized on tpyaz and tpy, respectively. The same pattern was observed for  $[4]^{2+}$  in CH<sub>3</sub>CN ( $E_{1/2} = -1.52$  V and -1.77 V). Here the signals are assignable to redox reactions localized on the two tpy ligands; *cf.* Figure 6, black.<sup>[10]</sup> More importantly, under CO<sub>2</sub> atmosphere, the

addition of a second electron to  $[3]^{2+}$  caused increased cathodic current at -1.70 V (*cf.* Figure 5, red).



Figure 5. Cyclic voltammograms of  $[3]^{2+}$  under Ar (black) and CO<sub>2</sub> (red) at a scan rate v = 100 mV s<sup>-1</sup>. Conditions: glassy carbon electrode, 1 mM  $[3]^{2+}$ , 0.1 M  $[Bu_4N][PF_6]$ , in CH<sub>3</sub>CN.



Figure 6. Cyclic voltammograms of [4]<sup>2+</sup> under Ar (black) and CO<sub>2</sub> (red, blue) at a scan rate  $v = 100 \text{ mV s}^{-1}$ . Conditions: glassy carbon electrode, 1 mM [4]<sup>2+</sup>, 0.1 M [Bu<sub>4</sub>N][PF<sub>6</sub>], in CH<sub>3</sub>CN.

In contrast, the addition of a second electron to  $[4]^{2+}$  (at -1.77 V) did not cause the same current effect (*cf.* Figure 6, red). These findings clearly indicate that the triazole moiety in  $[3]^{2+}$  enables direct interaction with CO<sub>2</sub> that leads to the increase in current near the second redox wave.

#### Bulk electrolysis of complexes [1]+-[4]<sup>2+</sup> under CO<sub>2</sub>

To evaluate the efficiency of complex  $[2]^+$  in CO<sub>2</sub> reduction near its first redox wave (threshold potential of -1.55 V), controlledpotential electrolysis was performed for both  $[1]^+$  and  $[2]^+$  at -1.55 V (see Table 1). Only trace amounts of CO were detected for both  $[1]^+$  (Table 1, entry 1) and  $[2]^+$  (Table 1, entry 2). It shows that addition of only one electron is not enough to drive CO<sub>2</sub> reduction for catalyst  $[1]^+$  or  $[2]^+$ . Recent reports, however, pointed out that addition of a proton source can facilitate two-electron and twoproton reduction of CO<sub>2</sub> to CO and HCOOH in CH<sub>3</sub>CN.<sup>[11]</sup> We

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consequently decided to add H<sub>2</sub>O as a proton source. CVs of [1]+ and [2]<sup>+</sup> were recorded under a CO<sub>2</sub> atmosphere with increasing concentration of H<sub>2</sub>O (cf. Figures S1 and S2, respectively). For both [1]<sup>+</sup> and [2]<sup>+</sup>, the catalytic current increased significantly and at the same time threshold potentials shifted to more positive values (-1.65 V and -1.55 V, for [1]<sup>+</sup> and [2]<sup>+</sup>, respectively, cf. Figure S1 and S2). This large enhancement of catalytic current is likely due to increased acidity in the CO<sub>2</sub>-saturated, aqueous solution (eq 1).<sup>[4b,11]</sup>

$$H_2O + CO_2 \iff H^+ + HOCO_2^-$$
 (1)

Controlled-potential electrolysis was then performed for [1]<sup>+</sup> and [2]+ at -1.55 V in CO2-saturated MeCN in presence of 5% and 10 %  $H_2O$  (see Table 1). To our surprise, complex [2]<sup>+</sup> showed a higher CO/HCOOH selectivity in presence of 5% H<sub>2</sub>O (Table 1, entry 4), whereas [1]<sup>+</sup> produced large amounts of hydrogen and minor quantities of CO (Table 1, entry 3). Moreover, current Table 1: Results of bulk electrolysis for complexes [1]+- [4]<sup>2+[a]</sup>

density (see Figure S6 and Table S2) and current efficiency (25.6 and 41.6% for [1]<sup>+</sup> and [2]<sup>+</sup>, respectively) was higher for [2]<sup>+</sup> compared to [1]<sup>+</sup>. With increasing water concentration (10% H<sub>2</sub>O in CH<sub>3</sub>CN), the tendency for CO<sub>2</sub> reduction over H<sub>2</sub> evolution decreased for both [1]<sup>+</sup> (Table 1, entry 5) and [2]<sup>+</sup> (Table 1, entry 6). Therefore, 5% H<sub>2</sub>O in CH<sub>3</sub>CN was considered the best solvent mixture for both catalysts. For comparison, controlled-potential electrolysis was also performed for [3]<sup>2+</sup> and [4]<sup>2+</sup> at -1.55 V in 5%  $H_2O$  in  $CH_3CN$ . Neither complex [3]<sup>2+</sup> (Table 1, entry 7) nor [4]<sup>2+</sup> (Table 1, entry 8) proved to be suitable catalysts under these reaction conditions. The discrepancy in catalytic behavior for [2]\* and [3]<sup>2+</sup> is probably caused by the different ligand structure. It is plausible to assume that, after electron induced dissociation of the Cl<sup>-</sup> ligand in [2]<sup>+</sup>, metal-centered CO<sub>2</sub> reduction is significantly slower in [3]<sup>2+</sup> due to the presence of an occupying, tridentate tpyligand compared to [2]+ with a vacant coordination site.

Entry	Catalyst	% of H <sub>2</sub> O in CH <sub>3</sub> CN	Coulombs consumed in 6	Product [µmol] <sup>[b]</sup>			Selectivity (CO / HCOO-)	Selectivity (CO + HCOO <sup>-</sup> / H <sub>2</sub> )
			h	СО	H <sub>2</sub>	HCOO-		
1	[ <b>1</b> ][PF <sub>6</sub> ]	0	2.1	0.25(2.2).	N.D	N.D.	-	-
2	[ <b>2</b> ][PF <sub>6</sub> ]	0	3	0.5(3.5)	N.D.	N.D	-	-
3	[ <b>1</b> ][PF <sub>6</sub> ]	5	18.3	15.9(17)	26.7(28.6)	8(8.6)	2	0.9
4	[ <b>2</b> ][PF <sub>6</sub> ]	5	25	49(38)	7.7(5.9)	4.8(3.6)	10.2	7
5	[ <b>1</b> ][PF <sub>6</sub> ]	10	23	18.3(15.4)	39.6(33.3)	12.1(10)	1.5	0.77
6	[ <b>2</b> ][PF <sub>6</sub> ]	10	29	51.6(34.4)	18.9(12.6)	10.4(6.9)	5	3.3
7	[ <b>3</b> ][PF <sub>6</sub> ] <sub>2</sub>	5	6	Trace	5(16)	Trace.	-	-
8	[ <b>4</b> ][PF <sub>6</sub> ] <sub>2</sub>	5	4	N.D	4(19)	N.D	-	-

[a] Controlled-potential electrolysis was carried out at -1.55 V (vs FeCp2\*0) using 1 mM complex in corresponding solvent system in the presence of 0.1 M [n-Bu<sub>4</sub>NI[PF<sub>6</sub>] as the supporting electrolyte: working electrode: glassy carbon: counter electrode: Pt. [b] current efficiency (%) given in parenthesis. Turnovers of the catalysts with respect to CO under 5% of H<sub>2</sub>O in CH<sub>3</sub>CN: [1]<sup>+</sup> = 0.71; [2]<sup>+</sup> = 2.5 after 6 h hours. For calculations of current efficiency and turnovers, please see supporting information.

Based on the experimental data, it is reasonable to propose the following reaction pathway for CO<sub>2</sub> activation by [2]<sup>+</sup> (Scheme 2): Cyclic voltammograms of [2]+ (Figure 4) displayed significant current enhancement near the first redox wave, while bulk electrolysis displayed no occurrence of significant CO2 reduction near the applied potential of -1.55 V. It shows that the addition of one electron to the tpyaz moiety enables weak interaction of the triazo-group with CO2. The second electron injection into [2]+then results in the appearance of strong catalytic current. At this point, the second electron is located at the bpy moiety causing the

release of Cl<sup>-</sup> and allowing CO<sub>2</sub> to react at the Ru-center.<sup>[4b]</sup> Addition of small amounts of water lowers the overpotential for CO2 reduction<sup>[4b,11]</sup> (Figure S1 and S2) due to CO2-assisted acidity increase in aqueous solutions (eq 1). Although the mechanism for CO<sub>2</sub> reduction by [2]<sup>+</sup> is not fully understood yet, it is clear from the obtained experimental data that the tpyaz moiety in [2]+ plays an important role in the initial CO2 activation stage due to weak interactions with CO2. More detailed investigations regarding these mechanistic steps are currently underway in our laboratory.



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Scheme 2. Proposed scheme for CO<sub>2</sub> activation by [2]\*. Red-highlighted ligand fragments indicate the one-electron-reduced state.

#### Conclusions

In summary, we have demonstrated that incorporating a triazole moiety in the ligand framework can significantly enhance the performance of CO<sub>2</sub> reduction by using Ru-polypyridyl complexes. Both CV and bulk electrolysis results evidently indicate that complex [2]<sup>+</sup> containing a triazole ring is more efficient and selective towards CO formation than [1]<sup>+</sup> which lacks the triazole. Further exploration of this moiety and related functional groups for more efficient Ru-catalysts is underway in our laboratory.

#### **Experimental Section**

#### Materials and methods

Complexes [1]<sup>+ [6]</sup> and [4]<sup>2+ [7]</sup> were synthesized according to literature reports and characterized by NMR and ESI-MS spectroscopy. Detailed synthetic procedures for complexes  $[2]^+$  and  $[3]^{2+}$  were described in the Supporting Information and characterized by NMR, ESI-MS, elemental crystallography. data and X-rav Tetra-n-butvlammonium hexafluorophosphate [n-Bu<sub>4</sub>N][PF<sub>6</sub>] was purchased from Tokyo Kasei Organic Chemicals and recrystallized from ethanol. CO2 was purchased from NIPPON EKITAN Corporation (research grade, 99.99% purity; < 3 ppm H<sub>2</sub>O) and used as received. All other chemicals (reagent grade) were obtained from common commercial suppliers and used as received. Airsensitive materials were prepared and manipulated using Schlenk techniques and/or an argon-filled glovebox (Glovebox Japan Inc., model number, GBJF100).

<sup>1</sup>H and <sup>13</sup>C NMR spectra were measured in CD<sub>3</sub>CN on a BRUKER AVANCE III spectrometer at 293 K. The chemical shifts are given in ppm relative to the residual solvent signal of CHD<sub>2</sub>CN ( $\delta$  1.94) or solvent signal of <sup>13</sup>CD<sub>3</sub>CN ( $\delta$  1.32).<sup>[12]</sup> Electrospray-ionization mass spectrometry (ESI-MS) was performed on a Thermo Fisher Scientific EXACTIVE instrument. Gaseous products were analyzed using a SHIMADZU GC-2014 gas chromatograph equipped with a thermal conductivity detector (TCD). Detection and quantification of the formate anion (HCOO<sup>-</sup>) were carried out by SHIMADZU Prominence HPLC analysis.

#### Electrochemistry

Cyclic voltammetry (CV) experiments were carried out using a onecompartment, three-electrode configuration, connected to a BAS ALS/CHI model 660A electrochemical analyzer. The electrode setup included a glassy carbon disc (0.071 cm<sup>2</sup>) working electrode that was polished with alumina (0.05  $\mu$ m) prior to use, a coil platinum wire as the counter electrode, and a Ag/AgNO<sub>3</sub> reference electrode, which was calibrated using FeCp<sub>2</sub> as the internal standard. Cyclic voltammograms were measured using 0.1 M [*n*-Bu<sub>4</sub>N][PF<sub>6</sub>] as the supporting electrolyte in either Ar- or CO<sub>2</sub>-saturated CH<sub>3</sub>CN (H<sub>2</sub>O/CH<sub>3</sub>CN in some cases) solutions at

room temperature. The controlled-potential electrolysis was performed in an H-type electrolysis cell with two compartments: one for a glassy carbon working electrode and the Ag/Ag+ reference electrode, and the other for the Pt counter electrode, which was separated from the working electrode by a Nafion membrane. Both compartments were made airtight by attaching silicon septa with vacuum grease. Initially, to each compartment was added 20 mL of a solution containing 0.1 M [n-Bu<sub>4</sub>N][PF<sub>6</sub>] as the supporting electrolyte. Afterwards, 1 mM of the corresponding complex was added to the working electrode compartment, and the mixture was stirred for 10 min. Both compartments were initially degassed by Ar saturation (15 min), before the compartment of the working electrode was saturated with 1 atm of CO2 for 20 min. The controlled-potential electrolysis was performed using a HOKUTO DENKO HZ-5000 potentiostat. During the electrolysis, gaseous aliquots (0.5 mL) were sampled from the headspace using a gas-tight syringe, and injected into the GC. Liquid samples (500 µL) were taken from the reaction mixture, before they were treated with a 0.1 M aqueous solution of NaOH (250 µL). The solutions were then evaporated to dryness on a rotary evaporator. The resulting solid was treated with 500 µL of water and filtered, before the quantities of HCOOH were measured using HPLC analysis. The quantification of H<sub>2</sub>, CO and HCOOH were carried out using a calibration curve (Figure S3,S4 and S5 respectively).

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