doi:10.1246/cl.2010.1134

Redox Behavior of Ruthenium(Bipyridine)(Terpyridine)(Carbonyl) Complex-modified Carbon Electrode and Reactivity toward Electrochemical Reduction of CO_2

Yuhei Tsukahara, Tohru Wada, and Koji Tanaka*

Coordination Chemistry Laboratories, Institute for Molecular Science, 5-1 Higashiyama, Myodaiji, Okazaki, Aichi 444-8787

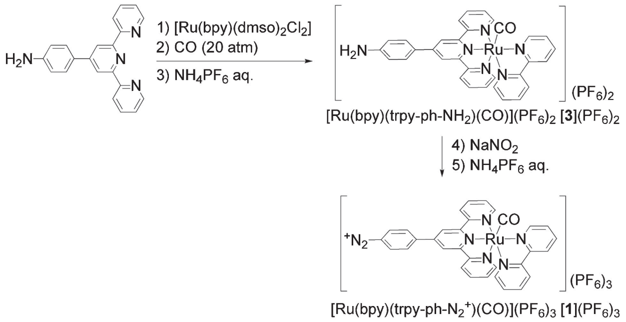
(Received August 9, 2010; CL-100680; E-mail: ktanaka@ims.ac.jp)

Electrochemical reduction of a diazonium complex $[Ru(bpy)(trpy\text{-}ph\text{-}N_2^+)(CO)](PF_6)_3$ ($[\mathbf{1}](PF_6)_3$) (bpy = 2,2′-bipyridine, trpy-ph-N_2^+ = 4-(2,2′:6′,2″-terpyridine-4′-yl)benzenediazonium) using a GC electrode forms multilayer films of the complexes on the electrode surface, on which the reduced form of the complex showed strong affinity toward CO_2.

Electrocatalytic reactions using functionalized electrodes modified with redox-active[1] molecular catalysts, or proteins[2] have led to supplementary advantages in terms of enhancement of catalytic efficiency because of minimizing the amounts of catalysts and facilitating electron transfer between catalysts and electrodes.[3] However, bonding strengths between electrode surfaces and catalyst molecules are not always strong enough to be utilized in electrocatalytic reductions. For example, self-assembled thiolate monolayers (SAMs) on gold surfaces have relatively narrow electrochemical potential windows and desorb at potentials more negative than −1.0 V (vs. SCE) in aqueous media.[4] In fact, modified electrodes with molecular catalysts have hardly been applied for electrochemical CO_2 reductions since electrolysis in those reactions are usually conducted at potentials more negative than −1.0 V. Among various methodologies to obtain functionalized electrodes modified with redox-active molecules, electrografting by irreversible reduction of diazonium compounds is a feasible process to form a strong C–C bonds between redox-active molecules and surfaces of carbon electrodes.[5]

We describe here modification of a ruthenium(bipyridine)(terpyridine)(carbonyl) framework on a carbon electrode with a C–C bond to clarify the reactivity of the complex embedded in the films toward electrochemical CO_2 reduction, since $[Ru(bpy)(trpy)(CO)](PF_6)_2$ ($[\mathbf{2}](PF_6)_2$) (trpy = 2,2′:6′,2″-terpyridine) has the ability to catalyze electrochemical reduction of CO_2 at −1.60 V (vs. Ag/Ag$^+$) in DMF/H_2O.[6]

A $[Ru(bpy)(trpy\text{-}ph\text{-}NH_2)Cl]Cl$ (trpy-ph-NH_2 = 4′-(4-aminophenyl)-2,2′:6′,2″-terpyridine) complex was obtained by reaction of $[Ru(bpy)(dmso)_2Cl_2]$ with trpy-ph-NH_2. Treatment of $[Ru(bpy)(trpy\text{-}ph\text{-}NH_2)Cl]Cl$ with CO (20 atm) followed by NH_4PF_6 afforded yellow crystals of $[Ru(bpy)(trpy\text{-}ph\text{-}NH_2)(CO)](PF_6)_2$ ($[\mathbf{3}](PF_6)_2$) in 63% yield. The reaction of $[\mathbf{3}](PF_6)_2$ with sodium nitrate gave a diazonium complex, $[Ru(bpy)(trpy\text{-}ph\text{-}N_2^+)(CO)](PF_6)_3$ ($[\mathbf{1}](PF_6)_3$), in 78% yield (Scheme 1). The IR spectra of $[\mathbf{1}](PF_6)_3$ showed characteristic $\nu(N{\equiv}N)$ and $\nu(C{\equiv}O)$ at 2282 and 2004 cm^{-1}, respectively.



Scheme 1. Synthesis of diazonium ruthenium complex $[\mathbf{1}](PF_6)_3$.

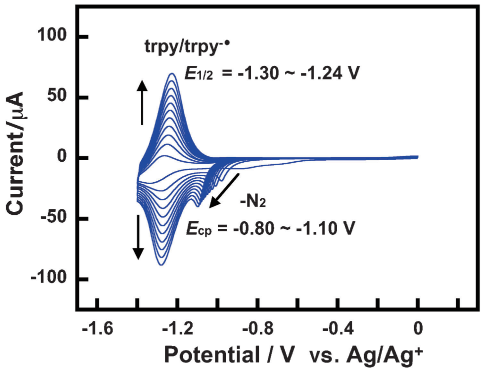


Figure 1. Repetitive CV of $[\mathbf{1}]^{3+}$ (10^{-3} M) at 50 mV s^{-1} in CH_3CN containing 0.1 M Bu_4NPF_6 using a GC electrode (S = 0.071 cm^2) in a potential region 0 and −1.4 V.

The cyclic voltammogram (CV) of $[\mathbf{1}](PF_6)_3$ using a glassy carbon (GC) electrode displays one irreversible cathodic peak at −0.80 V (vs. Ag/Ag$^+$) and one reversible (trpy/trpy$^{-\bullet}$) redox couple at $E_{1/2} = -1.30$ V in the first potential scan in CH_3CN (Figure 1). An analogous $[Ru(trpy)(trpy\text{-}ph\text{-}N_2^+)](PF_6)_3$ ($[\mathbf{4}](PF_6)_3$) exhibits one irreversible cathodic wave ($E_{pc} = -1.14$ V) assigned to reduction of diazonium and two reversible (trpy/trpy$^{-\bullet}$) redox couples ($E_{1/2} = -1.54$ and −1.70).[7] The −0.80 V cathodic wave of $[\mathbf{1}]^{3+}$, therefore, is associated with the irreversible reduction of the aryldiazonium affording N_2 and aryl radical that is responsible for formation of a C–C bond with the carbon electrode surface. Positive shift of the cathodic peak potential of $[\mathbf{1}]^{3+}$ compared with $[\mathbf{4}]^{3+}$ is attributed to an electron-withdrawing effect of CO in the former. Repetitive potential sweeps between −1.40 and 0 V caused an increase the peak currents of the $E_{1/2} = -1.30$ V redox couple of $[\mathbf{1}]^{3+}$ and positive shift of the redox potential to $E_{1/2} = -1.24$ V due to grafting of the complexes on the carbon electrode surface.

Modification on a GC electrode was carried out under the electrolysis of $[\mathbf{1}](PF_6)_3$ at −1.00 V in the presence of $TBAPF_6$ (0.1 M) in CH_3CN for 8 min. Then the carbon electrode was rinsed with CH_3CN to remove any physisorbed species. The CV of the modified glassy carbon electrode **1/GC** thus obtained exhibits the trpy/trpy$^{-\bullet}$ redox couple at $E_{1/2} = -1.25$ V, that is close to the value of $[\mathbf{2}](PF_6)_2$ ($E_{1/2} = -1.33$ V) in CH_3CN

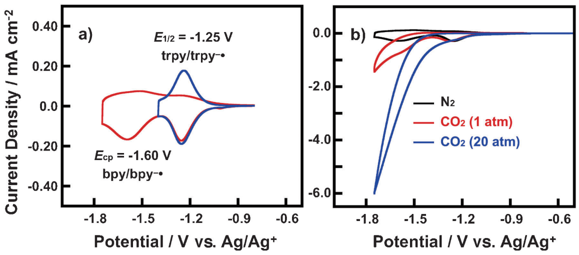


Figure 2. (a) CV of **1/GC** ($S = 0.071\,cm^2$) at $10\,mV\,s^{-1}$ in CH_3CN containing 0.1 M Bu_4NPF_6 in a potential region from −0.80 to −1.40 V (blue line) and from −0.80 to −1.75 V (red line) under N_2; (b) under N_2 (black line), under 1 atm of CO_2 (red line), and under 20 atm of CO_2 (blue line) in a potential region to −1.75 V.

(Figure 2a).[6] The IR reflection absorption spectroscopy (IRRAS) of the modified electrode **1/GC** showed characteristic peaks at 2009 and $862\,cm^{-1}$ assignable to $\nu(C\equiv O)$ and $\nu(PF_6^-)$, respectively, whereas any bands associated with $\nu(N\equiv N)$ completely disappeared (Figure S1[9]). These results demonstrate the retention of Ru(bpy)(trpy)(CO) framework on the surface of the carbon electrode.

The closed-packed monolayer coverage (Γ) of the complex on a perfectly flat surface is estimated to be ca. 1.6×10^{-10} $mol\,cm^{-2}$ based on the crystal structure of the amino derivative $[\mathbf{3}](PF_6)_2$ determined by X-ray analysis (Figure S2[9]). An actual coverage (Γ) of the complex was calculated as 3.1×10^{-8} $mol\,cm^{-2}$ from the area of the cathodic (and anodic) wave. The Γ value decreased only to $2 \times 10^{-9}\,mol\,cm^{-2}$ even when a highly oriented pyrolytic graphite (HOPG) with a basal plane was used in place of a GC plate, indicating formation of a multilayer film consisting of the Ru(bpy)(trpy)(CO) unit, as reported somewhere.[8] The multilayer film would be formed by a repetitive attack of Ru(trpy-ph$^\bullet$) generated in the irreversible reduction of $[Ru(bpy)(trpy\text{-}ph\text{-}N_2{}^+)(CO)]^{3+}$ to carbon on bpy or trpy of the adsorbed Ru(bpy)(trpy-ph)(CO) complexes on the carbon surface by considering that bpy would be located at the most outside layer of the modified film. An electrografting polyfilm, therefore, would consist almost entirely of an Ru(trpy-aryl)(bpy-Ru) bridge.

The anodic peak of the $E_{1/2} = -1.25\,V$ redox couple disappeared after the potential sweep is expanded to −1.75 V (Figure 2a). It is worthy of note that the CV of the homogeneous solution containing the analogous $[Ru(bpy)(trpy)(CO)]^{2+}$ $[\mathbf{2}]^{2+}$ in the same solvent exhibits one reversible (trpy/trpy$^{-\bullet}$) redox couple at −1.33 V and one irreversible cathodic peak of the (bpy/bpy$^{-\bullet}$) wave at −1.69 V that is caused by cleavage of the Ru–CO bond of $[\mathbf{2}]^0$.[6] The disappearance of anodic wave (trpy/trpy$^{-\bullet}$) of the **1/GC** after the potential sweep to −1.75 V, therefore, is associated with the Ru–CO bond cleavage caused by successive trpy and bpy localized reductions. The cathodic currents of the **1/GC** increased at potentials more negative than the irreversible cathodic (bpy/bpy$^{-\bullet}$) wave under 1 atm of CO_2. Furthermore, irreversible cathodic currents increased sixfold when the CV was measured under 20 atm of CO_2 (Figure 2b), indicating that the rate-determining step of the present electrochemical CO_2 reduction involves CO_2 attack at the Ru center.

Controlled-potential electrolysis using the **1/GC** (5×10^{-8} mol, surface area $S = 2\,cm^2$) at −1.70 (vs. Ag/Ag$^+$) under 1 atm of CO_2 in CH_3CN/H_2O (4:1 v/v) containing 0.1 M of $TBAPF_6$ for 0.5 h produced CO (0.9 µmol), HCOOH (0.3 µmol), and H_2 (1 µmol) with current efficiencies 30, 10, and 30%, respectively, but the cathodic currents dramatically decreased within 0.5 h.

Scanning electron micrographs (SEM) of the **1/GC** showed rough granular surface compared to those of unmodified GC (Figure S3[9]). After electrochemical reduction of CO_2 using the **1/GC**, the SEM images revealed disappearance of the rough granular surface in some part of the modified region due to partial detachment of the multilayer film from the GC surface. On the other hand, $[\mathbf{2}](PF_6)_2$ (1.0 mM) worked stably as a catalyst in electrochemical CO_2 reduction and produced CO and HCOOH at −1.70 V in CH_3CN/H_2O. Detachment of the multilayer film from the **1/GC** surface in the present study, therefore, may be caused mainly by collapse of the surface structure of the GC plate rather than degradation of the metal complex and fragmentation of the multilayer films during the CO_2 reduction. Taking into account achievement of a high current density ($6\,mA\,cm^{-1}$) of **1/GC** in the electrochemical CO_2 reduction under 20 atm of CO_2, methodological developments to depress detachment of redox active catalysts from electrode surfaces may open a new area in a utilization of CO_2 as a C1 resource.

We thank Mr. Takuya Iizuka and Dr. Shin-ichi Kimura (IMS) for IRRAS measurements and Mr. Satoru Nakao (IMS) for SEM measurements. This work was supported by the Grant-in-Aid for Scientific Research on Priority Areas (No. 20002005) from Ministry of Education, Culture, Sports, Science and Technology, Japan.

References and Notes

1 a) J. P. Collman, N. K. Devaraj, R. A. Decréau, Y. Yang, Y.-L. Yan, W. Ebina, T. A. Eberspacher, C. E. D. Chidsey, *Science* **2007**, *315*, 1565. b) J. J. Concepcion, J. W. Jurss, M. K. Brennaman, P. G. Hoertz, A. O. T. Patrocinio, N. Y. M. Iha, J. L. Templeton, T. J. Meyer, *Acc. Chem. Res.* **2009**, *42*, 1954.

2 a) T. W. Woolerton, S. Sheard, E. Reisner, E. Pierce, S. W. Ragsdale, F. A. Armstrong, *J. Am. Chem. Soc.* **2010**, *132*, 2132. b) M. Zayats, B. Willner, I. Willner, *Electroanalysis* **2008**, *20*, 583.

3 J.-M. Savéant, *Chem. Rev.* **2008**, *108*, 2348.

4 a) N. J. Brewer, S. Janusz, K. Critchley, S. D. Evans, G. J. Leggett, *J. Phys. Chem. B* **2005**, *109*, 11247. b) E. Cooper, G. J. Leggett, *Langmuir* **1998**, *14*, 4795. c) M. W. J. Beulen, M. I. Kastenberg, F. C. J. M. van Veggel, D. N. Reinhoudt, *Langmuir* **1998**, *14*, 7463.

5 a) D. Evrard, F. Lambert, C. Policar, V. Balland, B. Limoges, *Chem.—Eur. J.* **2008**, *14*, 9286. b) J. Pinson, F. Podvorica, *Chem. Soc. Rev.* **2005**, *34*, 429. c) M. Delamar, R. Hitmi, J. Pinson, J. M. Savéant, *J. Am. Chem. Soc.* **1992**, *114*, 5883.

6 a) H. Nagao, T. Mizukawa, K. Tanaka, *Chem. Lett.* **1993**, 955. b) H. Nagao, T. Mizukawa, K. Tanaka, *Inorg. Chem.* **1994**, *33*, 3415. c) K. Tanaka, D. Ooyama, *Coord. Chem. Rev.* **2002**, *226*, 211.

7 B. Jousselme, G. Bidan, M. Billon, C. Goyer, Y. Kervella, S. Guillerez, E. A. Hamad, C. Goze-Bac, J.-Y. Mevellec, S. Lefrant, *J. Electroanal. Chem.* **2008**, *621*, 277.

8 a) Y.-C. Liu, R. L. McCreery, *J. Am. Chem. Soc.* **1995**, *117*, 11254. b) J. K. Kariuki, M. T. McDermott, *Langmuir* **1999**, *15*, 6534.

9 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.