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Seven-coordinate Rhenium(III) Complexes with a Labile Coordination Site Assembled on Indium-doped Tin Oxide (ITO) Electrodes: Catalytic Reduction of Dioxygen to Hydrogen Peroxide

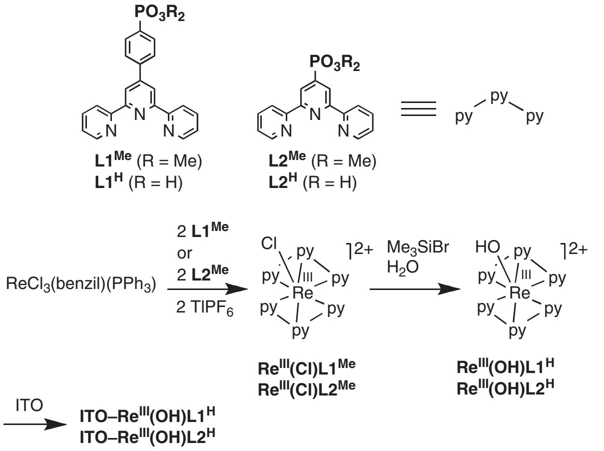
Hideki Sugimoto,*[1] Hiroyuki Tano,[2] Hiroyuki Miyake,[2] and Shinobu Itoh*[1]
[1]*Department of Material and Life Science, Division of Advanced Science and Biotechnology, Graduate School of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871*
[2]*Department of Chemistry, Graduate School of Science, Osaka City University, 3-3-138 Sugimoto-cho, Sumiyoshi-ku, Osaka 558-8585*

(Received May 17, 2010; CL-100476; E-mail: sugimoto@mls.eng.osaka-u.ac.jp, shinobu@mls.eng.osaka-u.ac.jp)

The complexes containing seven-coordinate bis(terpyridine)rhenium(III)(OH) moiety with phosphonic acid groups on the ligand have been synthesized and attached on indium-doped tin oxide electrodes. The modified electrodes show pH dependent cyclic voltammograms due to proton-coupled electron transfer and catalyze electrochemical reduction of dioxygen to hydrogen peroxide.

One of the most effective strategies in the development of novel molecular devices such as sensors and nanosized catalysts is to immobilize redox- and photoactive metal complexes on semiconductor electrodes by utilizing chemical bonds.[1] A number of transition-metal complexes such as ferrocene derivatives and polypyridyl complexes of $Re^{I}(CO)_2$,[2] Fe^{II},[3] Ru^{II},[4] Os^{II},[5] and Co^{III}[6] have been immobilized on electrodes and the electron- and charge-transfer processes between the complexes and electrodes have extensively been studied. However, modified electrodes that respond to external stimuli leading chemical reactions have been limited.[7]

Polypyridyl rhenium complexes exhibit unique properties among the polypyridyl metal complexes because the rhenium centers can adopt both 6- and 7-coordinate structures depending on the oxidation numbers.[8] Bis(terpyridine)rhenium and tris(bipyridyl)rhenium compounds are typical examples, where the rhenium(III) ions adopt a 7-coordinate structure including a monodentate anionic/neutral external ligand (X) to form $[Re^{III}X(\text{terpyridine})_2]^{n+}$ and $[Re^{III}X(\text{bipyridyl})_3]^{n+}$ ($n = 2$ or 3). On the other hand, the rhenium(I) and -(II) centers favor a six coordinate structure with no monodentate ligand.[8] Thus, polypyridyl rhenium complexes attached on an electrode are expected to show a unique electrochemical function using the 7th labile coordination site. However, such polypyridyl rhenium(II)/(III) complexes immobilized on an electrode have yet to be reported. Here, we describe synthesis of 7-coordinate hydroxobis(terpyridine)rhenium(III) complexes bearing $-PO(OH)_2$ groups on the ligand for immobilization on ITO (indium-doped tin oxide) electrodes and their catalytic activity in O_2 reduction (Scheme 1).



Scheme 1. Synthetic procedures for preparations of the rhenium complexes and the modified electrodes.

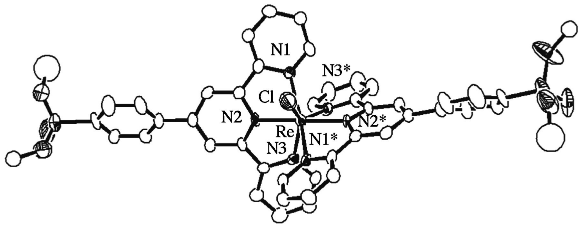


Figure 1. ORTEP drawing of the cationic part of $\mathbf{Re^{III}(Cl)L1^{Me}}$ showing 50% probability thermal ellipsoids. The hydrogen atoms are omitted for clarity.

Ligands $\mathbf{L1^{Me}}$ and $\mathbf{L2^{Me}}$ were prepared by following the procedures for the synthesis of the Et derivative of $\mathbf{L2^{Me}}$.[9–11] The seven-coordinate rhenium(III) complexes, $[Re^{III}Cl(\mathbf{L1^{Me}})_2](PF_6)_2$ ($\mathbf{Re^{III}(Cl)L1^{Me}}$)[12] and $[Re^{III}Cl(\mathbf{L2^{Me}})_2](PF_6)_2$ ($\mathbf{Re^{III}(Cl)L2^{Me}}$),[13] were obtained by the reactions of $Re^{III}Cl_3(benzil)(PPh_3)$ with the corresponding ligands in 10 and 46% yields, respectively. The crystal structure of $\mathbf{Re^{III}(Cl)L1^{Me}}$ is shown in Figure 1.[14] The rhenium center is coordinated by six nitrogen atoms from two $\mathbf{L1^{Me}}$ ligands and one chloride. The N2–Re–N2* angle is 177.5(5)°, indicating that the rhenium center adopts a pentagonal-bipyramidal stereochemistry with a N2–Re–N2* axis. Then, the complexes were treated with Me_3SiBr to hydrolyze the PO_3Me_2 groups to give the PO_3H_2 derivatives. Peak clusters appearing in the FAB-mass spectra of the isolated red powders were consistent with the formulas of $\{[Re(OH)(\mathbf{L1^{H}})_2] - 3H\}^+$ ($m/z = 979$) and $\{[Re(OH)(\mathbf{L2^{H}})_2] - 3H\}^+$ ($m/z = 827$), and the absorption spectra in H_2O ($\lambda_{max} = 512\,nm$, $\varepsilon = 15000\,M^{-1}\,cm^{-1}$ for the former and $\lambda_{max} = 508\,nm$, $\varepsilon = 10100\,M^{-1}\,cm^{-1}$ for the latter) were closely similar to that of $[Re^{III}(OH)(\text{terpyridine})_2](PF_6)_2$ ($\lambda_{max} = 512\,nm$, $\varepsilon = 13110\,M^{-1}\,cm^{-1}$).[8] This indicates that ligand substituion of Cl^- by OH^- took place to yield $[Re^{III}(OH)(\mathbf{L1^{H}})_2]Br_2$ ($\mathbf{Re^{III}(OH)L1^{H}}$)[15] and $[Re^{III}(OH)(\mathbf{L2^{H}})_2]Br_2$ ($\mathbf{Re^{III}(OH)L2^{H}}$)[16] upon the hydrolytic reactions using Me_3SiBr.

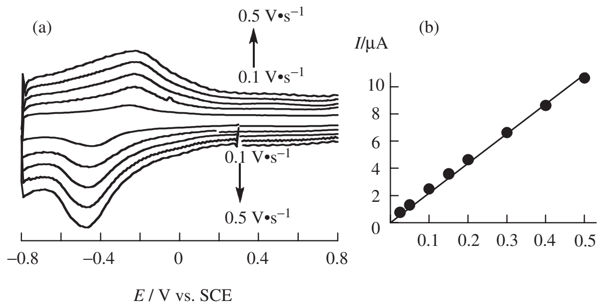


Figure 2. (a) Cyclic voltammograms of ITO electrode modified with **Re^{III}(OH)L1^{H}** measured at scan rate: 0.1, 0.2, 0.3, 0.4, and 0.5 V s^{-1} in a NaH_2PO_4–K_2HPO_4 buffer solution (pH 6.9). (b) Linear correlation of the current against the scan rate.

Modified ITO electrodes were prepared by dipping ITO electrodes into aqueous solutions of the hydrolyzed complexes (1.0×10^{-4} M).[17] The electron transfer between the attached complexes and the ITO electrode surface was analyzed by cyclic voltammetry (CV). Both electrodes exhibited one irreversible redox wave, rather than the surface confined reversible redox process, at −0.34 V vs. SCE assignable to the Re(III)/Re(II) redox at pH 6.9 in a NaH_2PO_4–K_2HPO_4 buffer solution (Figure 2). The CV profiles suggest that a chemical reaction followed the electrochemical reduction similar to those of seven-coordinate bis(terpyridine)rhenium(III)X complexes (X = monodentate ligand) that showed a quasi-reversible redox wave due to a formation of a six-coordinate bis(terpyridine)-rhenium(II) species upon the reduction.[8] The intensities of the anodic and cathodic currents were proportional to the scan rate up to 0.5 V s^{-1}, indicative of immobilization of the complexes on the ITO electrode. The surface coverage for the electrodes with the complexes were calculated to be 5.8×10^{-11} mol cm^{-2} for **ITO–Re^{III}(OH)(L1^{H})** and 0.9×10^{-11} mol cm^{-2} for **ITO–Re^{III}(OH)(L2^{H})** from Coulomb numbers consumed in the electrolysis at −0.6 V and the electrode areas. The limiting surface coverage of the ITO electrodes with the rhenium complexes were roughly estimated as 1.4×10^{-10} mol cm^{-2} by assuming that **Re^{III}(OH)L1^{H}** has a tetragonal structure and the structures are packed on a flat surface.[18] Since **Re^{III}(OH)L1^{H}** was well assembled on the ITO electrode than **Re^{III}(OH)L2^{H}**, ITO electrode with **Re^{III}(OH)L1^{H}** was employed for following experiments.

The pH dependence of CV of **ITO–Re^{III}(OH)L1^{H}** was then investigated (Figure S1 in the Supporting Information).[23] Whereas the E^{pc} value for the Re(III)/(II) process was hardly changed in a pH region from 4 to ca. 8, E^{pc} value moved to negative direction with a slope of −0.059 V/pH as pH of the solution increased from pH 8 to 11.5 (Figure 3).[19] This indicates that the Re^{III}(OH) species shows acid–base equilibrium to provide a Re^{III}(OH_2) species and the pK_a value is 8.0. The Re^{III}(OH) species is reduced to a Re^{II}(OH_2) complex above pH 8.0 by proton-coupled electron transfer on the ITO electrode.[20] A combination of the irreversible redox process which suggests a change of a coordination number of the rhenium center (from 7 to 6), and the pH dependent E^{pc} value indicates that a six coordinate bis(**L1^{H}**)rhenium(II) center is generated by dissociation of the aqua ligand from the seven-coordinate bis(**L1^{H}**)Re^{II}(OH_2) center formed by electrochemical reduction of the bis(**L1^{H}**)Re^{III}(OH/OH_2) complex (Scheme 2).

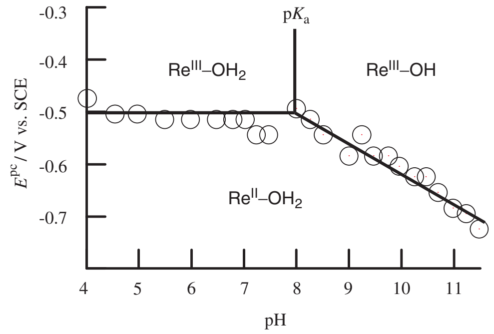
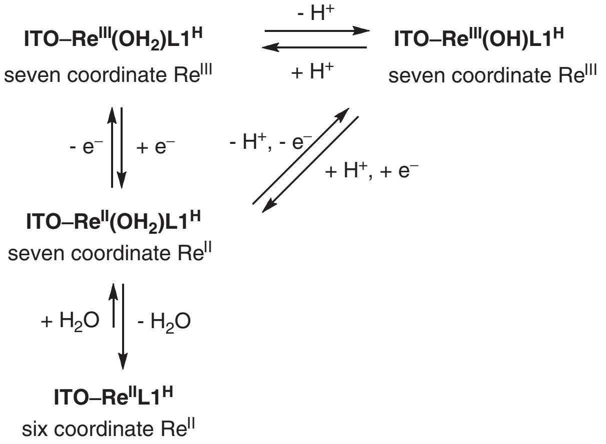


Figure 3. A plot of the E^{pc} value (Re(III)/Re(II) process) of **ITO–Re^{III}(OH)L1^{H}** against pH of the solution at 0.1 V s^{-1}.



Scheme 2. Proposed redox behavior coupled with proton–electron transfers and the coordination number change of the rhenium center assembled on ITO electrode.

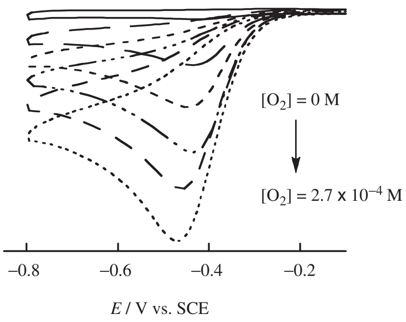


Figure 4. CVs of **ITO–Re^{III}(OH)L1^{H}** at pH 6.9 in a solution containing various concentrations of dioxygen recorded at 0.1 V s^{-1}.

Notably, the current intensity or area for the cathodic process of **ITO–Re^{III}(OH)L1^{H}** increased dramatically as the concentration of dioxygen dissolved in the buffer solution of pH 6.9 increased as indicated in Figure 4. Such increase of the cathodic current was not observed for an ITO electrode itself without **Re^{III}(OH)L1^{H}** under the same conditions. Furthermore, the original CV was regenerated by bubbling dinitrogen gas into

$$O_2 + 2H^+ + 2e^- \xrightarrow{\text{ITO–Re}^{\text{III}}\text{(OH)L1}^{\text{H}}} H_2O_2$$

Scheme 3. Reduction of dioxygen to hydrogen peroxide catalyzed by **ITO–Re^{III}(OH)L1^H** at pH 6.9.

the solution. The CV changes observed here could be attributed to catalytic reduction of dioxygen by the electrode. Bulk electrolysis of the solution saturated with dioxygen gas was done at −0.55 V using **ITO–Re^{III}(OH)L1^H** as a working electrode (5.0×10^{-11} mol of the complex has been assembled on the electrode). The Coulomb number consumed was proportional to time spent for the electrolysis (at least 360 min). Upon addition of KI to the final solution after 6 h, the solution changed in color from colorless to brown. The UV spectrum was identical with that of I_3^-, indicating that the electrolysis yielded hydrogen peroxide, H_2O_2.[22] From the mol number of H_2O_2 calculated from the molar coefficient of the absorbance of I_3^- ($\lambda_{max} = 361$ nm, $\varepsilon = 2.5 \times 10^4$ M^{-1} cm^{-1}) and Coulomb number consumed (0.17 C), a current efficiency and a turnover number for the catalytic reduction (Scheme 3) were determined to be 40% and 6.4×10^3, respectively. It is suggested that the catalytic reduction begins by coordination of dioxygen to the six coordinate rhenium(II) center and the resultant rhenium(III)–superoxo species may undergo successive reductions coupled with protonaion to provide H_2O_2.

In summary, this work has reported the preparation of ITO electrodes modified with seven coordinate bis(terpyridine)-rhenium(III)(OH) complexes and the effective catalytic activity toward reduction of O_2 to H_2O_2 in H_2O.

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11. **L1^{Me}**; ^{1}H NMR ($CDCl_3$): δ 8.75 (s, 2H), 8.69 (d, 2H), 8.02–7.94 (m, 4H), 7.90 (td, 2H), 7.38 (ddd, 2H), 3.81 (d, 6H). **L1^{Me}**; ^{1}H NMR ($CDCl_3$): δ 8.84 (d, 2H), 8.74 (d, 2H), 8.61 (d, 2H), 7.88 (td, 2H), 7.35 (ddd, 2H), 3.87 (d, 6H).
12. ^{1}H NMR (CD_3CN): δ 9.62 (s, 2H), 9.38 (s, 2H), 9.25 (d, 2H), 8.79 (d, 2H), 8.34–8.27 (m, 4H), 8.19–8.11 (m, 8H), 7.52 (d, 2H), 7.12 (t, 2H), 7.02 (m, 4H), 3.82 (d, 12H). Anal. Calcd for **Re^{III}(Cl)L1^{Me}**•3H_2O: C, 39.45; H, 3.31; N, 6.00%. Found: C, 39.19; H, 3.35; N, 6.18%.
13. ^{1}H NMR (CD_3CN): δ 9.54 (ddd, 2H), 9.32–9.18 (m, 4H), 8.75 (dd, 2H), 8.22–8.09 (m, 4H), 7.52 (dd, 2H), 7.14–7.07 (m, 2H), 7.05–6.95 (m, 4H), 3.99 (ddd, 12H).
14. Crystal data for **Re^{III}(Cl)L1^{Me}**•2H_2O: fw 1414.42, $P2/c$, $a = 15.605(3)$, $b = 8.9741(17)$, $c = 19.470(4)$ Å, $V = 2707.7(9)$ Å^3, $Z = 2$, 7164 independent reflections, 4198 reflections used ($I > 3\sigma(I)$, $R_1 = 0.0675$, $wR_2 = 18.05$.
15. ^{1}H NMR (CD_3OH): δ 9.87 (s, 2H), 9.66 (s, 2H), 9.46 (d, 2H), 9.03 (d, 2H), 8.43–8.39 (m, 4H), 8.22–8.15 (m, 8H), 7.65 (d, 2H), 7.26–7.17 (m, 4H), 7.10 (t, 2H). UV–vis (H_2O) λ_{max}: 512 nm ($\varepsilon = 15000$ M^{-1} cm^{-1}).
16. ^{1}H NMR (CD_3OH): δ 9.67 (d, 2H), 9.43 (d, 2H), 9.32 (d, 2H), 8.29 (d, 2H), 8.25–8.15 (m, 4H), 7.65 (d, 2H), 7.19–7.10 (m, 6H). UV–vis (H_2O) λ_{max}: 508 nm ($\varepsilon = 10100$ M^{-1} cm^{-1}).
17. Before surface modification, each ITO electrode was washed with a 5:1:1 solution of H_2O, H_2O_2, and NH_4OH and thoroughly rinsed with purified water. After heating at 120 °C for 60 min, the electrode was cooled and stored under dry dinitrogen.
18. The area of base of the tetragonal structure was estimated from the bond lengths and angles of the crystal structure of **Re^{III}(Cl)L1^{Me}** and size of the anions were neglected.
19. Since the Re(III)/Re(II) process was observed as a quasi-reversible process, the potential for E^{pc} was employed for the plot.
20. The pK_a value of [Re^{III}(OH)(terpyridine)$_2$](PF$_6$)$_2$ was calculated to be 1.4(8) from the kinetic study for substitution of the hydroxo group by NCS$^-$ ion.[21] However, the pK_a value obtained in this study appears to be more reasonable for seven-coordinate metal(III) complexes on the basis of a comparison with the pK_a values for the six-coordinate octahedral metal(III) complexes with one aqua ligand (ca. 3–4). A coordinating aqua ligand in a complex with increasing coordination number (6 to 7) would be weakly bound to the metal center and the pK_a value would be higher.
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23. Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.