Synthesis of A New Terpyridine Ligand Combined with Ruthenium(II) Complex and its Usage in the Stepwise Fabrication of Complex Polymer Wires on Gold

*Yoshiki Ohba, Katsuhiko Kanaizuka, Masaki Murata, Hiroshi Nishihara**

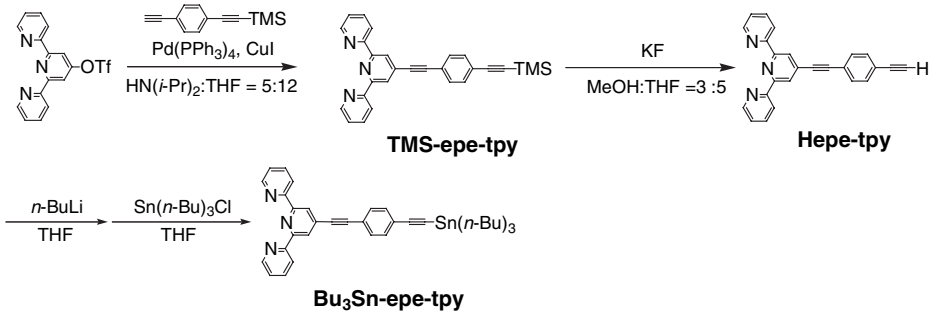
Summary: A ruthenium complex-combined terpyridine ligand, tpyRu(dpp)-(epe)-tpyPF_6, was synthesized. Stepwise coordination reactions at the gold surface using this ligand gave Co-Ru hetero-metal complex wires, [**1Co1Ru**], which underwent reversible redox reactions of both redox complex units.

Keywords: cyclic voltammogram; electrochemistry; ruthenium complex; terpyridine complex

Introduction

How to immobilize and assemble molecular wires on electrodes in a controlled manner to construct a designed molecular network is an important fundamental issue in the development of molecular electronics. We have recently reported the construction of one-dimensional redox complex polymer wires on a gold surface[1]. In this method, stepwise and alternative connection of a bis(terpyridine) linear bridging ligand and a metal ion, forming a hexadentate octahedral complex, can give linear polymer chains with a desired number of metal complex units and with a desired sequence of different metal complexes. One of the valuable metals forming octadentate polypyridine complexes is ruthenium, as ruthenium(II) complexes such as $[Ru(bpy)_3]^{2+}$ are redox-active and photoluminescent[2–4], and are utilizable in dye-sensitized solar cells[5–8]. A molecular wire with a ruthenium polypyridine complex may show photofunctionalities such as photo-electron conversion and electroluminescence if appropriate redox potential steps can be arranged around the ruthenium complex in the molecular wire. It is not easy, however, to connect the ruthenium ion at the surface in the stepwise coordination process to construct molecular wires, as the rate constant of complexation of a ruthenium ion with polypyridine ligands is very slow. We therefore employ a terpyridine ligand containing a ruthenium complex in the surface construction of complex polymer wires, and have in the present study synthesized a new terpyridine ligand having a (dipyridylphenyl)(terpyridine)ruthenium complex, $[(tpy)Ru(dpp\text{-}epe\text{-}tpy)]PF_6$. This dpp complex was selected because its Ru^{III}/Ru^{II} redox potential is less positive than that of $[Ru(bpy)_3]^{3+/2+}$ or $[Ru(tpy)_2]^{3+/2+}$[9,10], and it therefore can undergo stable redox reactions without irreversible oxidation of Au-thiolate when it is fixed on Au. Using this ligand, we fabricated a $Co(tpy)_2$-(dpp)Ru(tpy) dinuclear complex wire by the stepwise coordination method on a gold electrode. The electrochemical behavior of this molecular wire on gold is described in this paper.

Department of Chemistry, School of Science, The University of Tokyo, Tokyo 113-0033, Japan
E-mail: nishihara@chem.s.u-tokyo.ac.jp



Scheme 1.

Experimental Section

Synthesis

4′-(4-(Trimethylsilylethynyl)phenyl)-ethynyl-2,2′;6′,2″-terpyridine (TMS-epe-tpy) (Scheme 1)

All manipulations were carried out under nitrogen. Trifluoromethanesulfonic acid 2,2′;6′,2″-terpyridin-4′-yl ester[11] (527 mg, 1.38 mmol), (4-ethynylphenyl)ethynyl-trimethylsilane[12] (268 mg, 1.35 mmol), $Pd(PPh_3)_4$ (83.2 mg, 0.072 mmol) and CuI (14.2 mg, 0.074 mmol) were dissolved in diisopropylamine-THF (12:5 in v/v) and stirred at room temperature for 12 h. The solvent was evaporated, and the residue was purified by alumina column chromatography with hexane-chloroform (1:1 in v/v) as an eluent and further with preparative HPLC using JAIGEL-1H and 2H columns and chloroform as an eluent. TMS-epe-tpy was obtained as a white powder: yield 275 mg (46%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (ddd, $J = 4.7, 1.7, 0.8$ Hz, 2H, tpy), 8.63 (ddd, $J = 7.9, 1.0, 0.8$ Hz, 2H,tpy), 8.58 (s, 2H, tpy), 7.88 (ddd, $J = 7.9, 7.6, 1.7$ Hz, 2H, tpy), 7.49 (m, 4H, Ph), 7.36 (ddd, $J = 7.6, 4.7, 1.0$ Hz, 2H, tpy), 0.27 (s, 9H, TMS).

4′-(4-Ethynylphenyl)ethynyl-2,2′;6′,2″-terpyridine (Hepe-tpy) (Scheme 1)

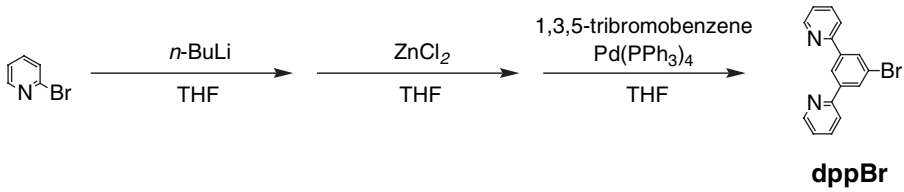
A mixture of TMS-epe-tpy (367 mg, 0.854 mmol) and KF (81 mg, 1.39 mmol) in methanol-THF (3:5 in v/v, 100 mL) was stirred for 12 h. The solvent was evaporated, and the residue was purified by alumina column chromatography with hexane-chloroform (2:1 in v/v) as an eluent. White powder of Hepe-tpy was obtained: yield 305 mg (95.8%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.70 (ddd, $J = 4.9, 1.9, 0.9$ Hz, 2H, Py), 8.63 (dt, $J = 8.1, 1.0$ Hz 2H, Py), 8.59 (s, 2H, Py), 7.90 (td, $J = 7.7, 1.8$ Hz, 2H, Py), 7.27 (d, $J = 8.7$ Hz, 2H, Ph), 7.24 (d, $J = 8.7$ Hz, 2H, Ph), 7.38 (ddd, $J = 7.5, 4.8, 1.2$ Hz, 2H, tpy), 2.95 (s, 1H).

4′-(4-(Tributylstannylethynyl)phenyl)-ethynyl-2,2′;6′,2″-terpyridine (Bu_3Sn-epe-tpy) (Scheme 1)

All manipulations were carried out under nitrogen. First, 140 mg (0.392 mmol) of Hepe-tpy was dissolved in THF (200 mL). To the solution a 1.6 M *n*-BuLi hexane solution (0.4 mL) was added at −78 °C and stirred for 2 h, after which 480 mg (1.47 mmol) of Bu_3SnCl was added at −78 °C and stirred for 30 min. The solvent was evaporated, and the residue was dissolved in dichloromethane and filtered. The solvent was evaporated from the filtrate to yield 289 mg of the mixture of Bu_3Sn-epe-tpy and Bu_3SnCl. The mole ratio of Hepe-tpy and Bu_3Sn-epe-tpy was 3:17 based on the ^{1}H NMR spectrum. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (ddd, $J = 4.8, 1.7, 1.0$ Hz, 2H, tpy), 8.64 (ddd, $J = 7.9, 1.1, 1.0$ Hz, 2H, tpy), 8.58 (s, 2H, tpy), 7.89 (ddd, $J = 7.9, 7.6, 1.7$ Hz, 2H, tpy), 7.54 (d, $J = 8.5$ Hz, 2H, Ph), 7.45 (s, $J = 8.5$ Hz, 2H, Ph), 7.37 (ddd, $J = 7.4, 4.8, 1.0$ Hz, 2H, tpy), 1.7–0.8 (m, 27H, Bu).

1-Bromo-3,5-(di(2-pyridyl)benzene (dppBr) (Scheme 2)

All manipulations were carried out under nitrogen. A 1.6 M *n*-BuLi solution in hexane

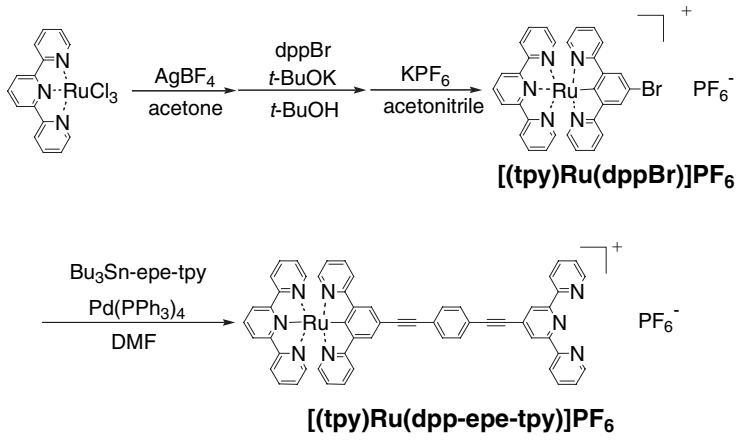


Scheme 2.

(60 mL) was added to the stirred solution of 2-bromopyridine (10.0 g, 63.3 mmol) in THF (500 mL) at −78 °C and stirred for 30 min. $ZnCl_2$ (20.7 g, 152 mmol) was added to the solution with stirring at 0 °C. After 30 min, 1,3,5-tribromobenzene (10.0 g, 31.7 mmol) and $Pd(PPh_3)_4$ (1.02 g, 0.883 mmol) was added to the solution and refluxed for 2 h. The solvent was evaporated, and the residue was dissolved in dichloromethane. After washing with water, the solution was concentrated and purified by alumina column chromatography with hexane-chloroform (2:1 in v/v) as an eluent, affording 1.49 g (15%) of dppBr as a white powder. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (ddd, $J = 4.8$, 1.7, 1.1 Hz, 2H, Py), 8.55 (t, $J = 1.6$ Hz, 1H, Ph), 8.22 (d, $J = 1.7$ Hz, 2H, Ph), 7.83 (ddd, $J = 7.9$, 1.4, 1.1 Hz, 2H, Py), 7.79 (ddd, $J = 7.4$, 7.4, 1.7 Hz, 2H, Py), 7.29 (ddd, $J = 6.8$, 4.8, 1.4Hz, 2H, Py). Anal. Calcd for.: $C_{16}H_{10}N_2Br$; C, 81.53; H, 4.89; N 13.58%. Found: C, 81.30; H, 5.09; N, 13.39%.

(4-Bromo-3,5-di-2-pyridylphenyl)(2,2′; 6′,2″-terpyridine)ruthenium(II) hexafluorophosphate ([(tpy)Ru(dppBr)]PF_6) (Scheme 3)

All manipulations were carried out under nitrogen. A mixture of (tpy)$RuCl_3$ (507.6 mg, 1.15 mmol) and $AgBF_4$ (720 mg, 3.70 mmol) in acetone (100 mL) was refluxed for 2 h. The solution was filtered, and the solvent of the filtrate was evaporated. The product was added to a stirred solution of dppBr (378.6 mg, 1.22 mmol) in *t*-BuOH (150 mL), after which *t*-BuOK (138.3mg, 1.23 mmol) was added to the solution. After refluxing for 12 h, the solvent was evaporated and the residue was purified by silica-gel column chromatography with sat.CH_3CN-KNO_3 aq (20:1 in v/v) as an eluent. The purple-band component was collected, and the solution was concentrated, followed by reprecipitation with a KPF_6 solution in CH_3CN. Recrystallization from CH_2Cl_2-hexane afforded purple crystals: yield 326 mg



Scheme 3.

(36%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.65 (d, $J = 8.0$ Hz, 2H, tpy), 8.31(ddd, $J = 8.1$, 1.4, 0.8 Hz, 2H, Py), 8.30 (s, 2H, dpp), 8.27 (t, $J = 8.0$ Hz, 1H, tpy), 8.02 (ddd, $J = 8.1$, 1.3, 0.8 Hz, 2H, dpp), 7.66 (ddd, $J = 8.1$, 7.5, 1.5 Hz, 2H, tpy), 7.58 (ddd, $J = 8.1$, 7.3, 1.5 Hz, 2H, dpp), 7.14 (ddd, $J = 5.7$, 1.5, 0.8 Hz, 2H, tpy), 6.99 (ddd, $J = 5.6$ 1.5, 0.8 Hz, 2H, dpp), 6.90 (ddd, $J = 7.5$, 5.7, 1.4 Hz, 2H, tpy), 6.66 (ddd, $J = 7.3$, 5.6, 1.3 Hz, 2H, dpp).

(2,2′;6′,2″-Terpyridine)((4-(4-(4′-2,2′;6′,2″-terpyridyl)ethynylphenyl)-ethynyl)-3,5-di-2-pyridylphenyl)-ruthenium(II) hexafluorophosphate ([(tpy)Ru(dpp-epe-tpy)]PF_6) (Scheme 3)

All manipulations were carried out under nitrogen. Bu_3Sn-epe-tpy (215 mg, 0.333 mol), and $Pd(PPh_3)_4$ (20.3 mg, 0.018 mmol) were dissolved in DMF (100 mL), to which a solution of [(tpy)Ru(dppBr)]PF_6 (99.7 mg, 0.126 mmol) in DMF (50 mL) was added with stirring at 100 °C. After heating for 24 h, the solvent was evaporated and the residue was purified by reprecipitation from dichloromethane/hexane, affording a purplish red solid. Yield, 70.3 mg (52%). ^{1}H NMR (400MHz, CD_2Cl_2) δ 9.07 (d, $J = 8.1$ Hz, 2H, tpy), 8.64 (d, $J = 8.1$ Hz, 2H, tpy), 8.44 (s, 2H, tpy), 8.38 (s, 2H, dpp), 8.31 (d, $J = 8.0$ Hz, 2H, tpy), 8.28 (ddd, $J = 8.0$, 1.4, 0.5 Hz, 2H, tpy), 8.27 (t, $J = 8.0$ Hz, 1H, tpy), 8.15 (dd, $J = 8.0$, 7.8 Hz, 2H, tpy), 8.11 (ddd, $J = 7.3$, 1.3, 0.6 Hz, 2H, dpp), 7.76 (s, 4H, Ph), 7.74 (dd, $J = 7.8$, 5.1 Hz, 2H, tpy) 7.67 (ddd, $J = 8.0$, 7.6, 1.5 Hz, 2H, tpy), 7.62 (ddd, $J = 7.5$, 7.3, 1.4 Hz, 2H, dpp), 7.20 (ddd, $J = 5.7$, 1.5, 0.5 Hz, 2H, tpy), 6.99 (ddd, $J = 5.7$, 1.4, 0.6 Hz, 2H, dpp), 6.93 (ddd, $J = 7.6$, 5.7, 1.4 Hz, 2H, tpy), 6.68 (ddd, $J = 7.5$, 5.7, 1.3 Hz, 2H, dpp). HRMS (ESI): calcd. for $C_{56}H_{35}N_8Ru$ $[M]^+$ 921.2043. Found: 921.2067.

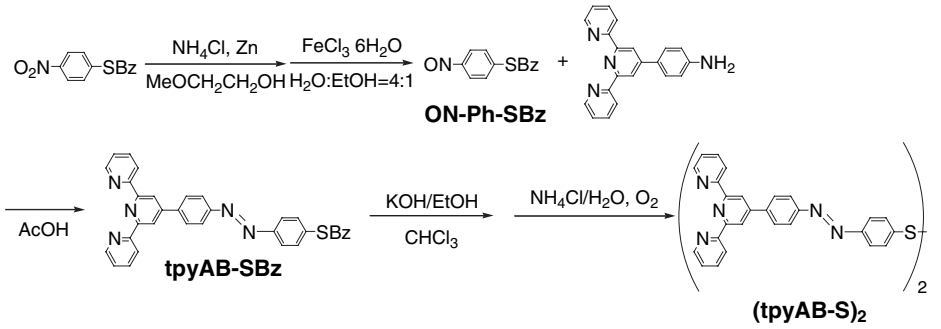
Thiobenzoic acid S-(4-nitrosophenyl)ester[13] (ON-Ph-SBz) (Scheme 4)

A saturated NH_4Cl (155 mg, 2.89 mmol) aqueous solution was added to the stirred solution of thiobenzoic acid S-(4-nitrophenyl)ester (500 mg, 1.93 mmol) in 2-methoxyethanol. Zn powder (321 mg, 4.91 mmol) was divided into five groups and added to the solution over 2 h with stirring at 40 °C. After 3 h, the solution was dropped into a stirring solution of $FeCl_36H_2O$ (1.31 g, 4.85 mmol) in water-ethanol (4:1 in v/v, 50 mL) at −10 °C. Yellow precipitate was filtered and cleaned with water. Yield, 374 mg (79.7%).

^{1}H NMR (400MHz, $CDCl_3$) δ 8.01 (d, $J = 8.1$ Hz, 2H, Ph), 7.94 (d, $J = 7.6$ Hz, 2H, Ph), 7.79 (d, $J = 8.1$ Hz, 2H, Ph), 7.64 (t $J = 7.6$ Hz, 1H, Ph), 7.50 (d, $J = 7.6$ Hz, 2H, Ph).

Thiobenzoicacid S-(4-(4-(4′-2,2′;6′,2″-terpyridyl)phenylazo)phenyl) ester (tpyAB-SBz) (Scheme 4)

4-(4′-2,2′;6′,2″-Terpyridyl)phenylamine (500 mg, 1.54 mmol) was added to acetic acid (40 ml). ON-Ph-SBz (373 mg, 1.53 mmol) was added to the solution and heated to



Scheme 4.

dissolve it. After allowing the solution to stand overnight, the solvent was vacuumed, and the remaining acetic acid was neutralized with sodium carbonate and the product was extracted with dichloromethane. White crystals afforded by recrystallization from dichloromethane/ethanol were filtered and washed with ethanol. Yield, 342 mg (40.6%). ^{1}H NMR (400MHz, $CDCl_3$) δ 8.80 (s, 2H, Ph), 8.74 (d, J = 4.9 Hz, 2H, Ph), 8.68 (d, J = 7.8 Hz, 2H, Ph), 8.08 (s, 4H, Ph), 8.06-8.02(m, J = 4H, Ph), 7.88(td, J = 7.8, 1.6 Hz, 2H, Ph), 7.69 (d, J = 7.6 Hz, 2H, Ph), 7.63 (t, J = 7.6 Hz, 1H, Ph), 7.50 (t, J = 7.6 Hz, 2H, Ph) 7.36 (ddd, J = 7.8, 7.6, 1.1 Hz, 2H, Ph).

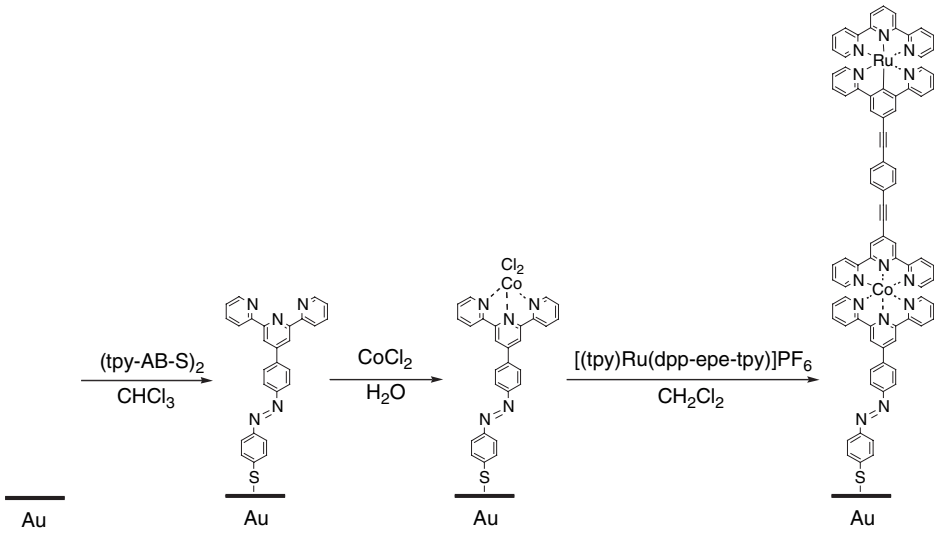
Anal. Calcd. for: $C_{34}H_{23}N_5OS$; C, 74.30; H, 4.22; N, 12.74%. Found: C, 74.00; H, 4.29; N, 12.72%.

Bis((4-(4′-2,2′;6′,2″-terpyridyl)phenylazo)phenyl)disulfide (tpyAB-S)$_2$ (Scheme 4)

TpyAB-SBz (500 mg, 0.910 mmol) was added to chloroform (30 ml), and the solution was dropped into a stirred solution of KOH (511 mg, 9.11 mmol) in ethanol (30 ml). The dark red solution was stirred for 3 h, after which a saturated NH_4Cl aqueous solution (40 ml) was added and stirred for an additional 16 h. The organic layer was washed with water (40 ml) four times, dried with sodium sulfate, and filtered. The solution was concentrated and purified by alumina column chromatography with chloroform as an eluent, affording (tpyAB-S)$_2$ as an orange powder with a yield of 321 mg (79.3%). ^{1}H NMR (400MHz, $CDCl_3$) δ 8.79 (s, 4H, Ph), 8.73(d, J = 4.9 Hz, 4H, Ph), 8.67 (d, J = 7.8 Hz, 4H, Ph), 8.04 (s, 8H), 7.93 (d, J = 8.6 Hz, 4H, Ph), 7.88 (td, J = 7.8, 1.6 Hz, 4H, Ph), 7.67 (d, J = 8.6 Hz, 4H, Ph), 7.35 (ddd, J = 7.8, 6.2, 1.6 Hz, 4H, Ph) Anal. Calcd. for $C_{54}H_{36}N_{10}S_2$: C, 70.80; H, 4.29; N, 15.29, S,7.00%. Found: C, 70.90; H, 4.18; N, 15.06, S, 7.14%.

Preparation of Co(tpy)$_2$-Ru(tpy)(dpp) complex wires, [1Co1Ru], on the gold electrode [1]. (Scheme 5)

First, Au/mica (annealed with hydrogen flame) was immersed in a chloroform solution of 0.1 mM (tpyAB-S)$_2$ for 10 min. The plate was then washed with chloroform and dried by nitrogen blow. Next, the plate was



Scheme 5.
The stepwise coordination method to prepare [**1Co1Ru**].

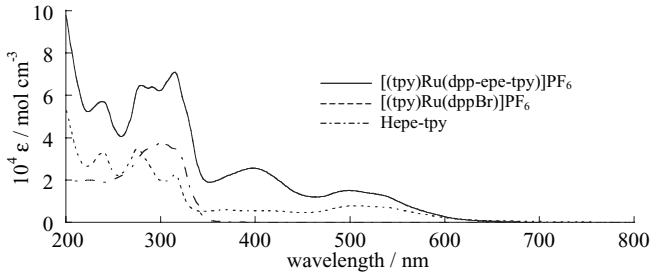


Figure 1.
UV-vis spectrum of Hepe-tpy, [(tpy)Ru(dpp)Br]PF_6 and [(tpy)Ru(dpp-epe-tpy)]PF_6 in dichloromethane.

immersed in a 0.1 M $CoCl_2$ aq for 30 min, washed with water and ethanol, and then dried by nitrogen blow. To prepare the ruthenium complex film, the metal-terminated surface was immersed in a dichloromethane solution of [(tpy)Ru(dpp-epe-tpy)]PF_6 for 30 min.

Electrochemical Measurements

Cyclic voltammetry measurements were carried out in a standard one-compartment cell equipped with a platinum-wire counter electrode and an Ag/Ag^+ reference electrode under Ar with a BAS CV-50W voltammetric analyzer. The cross-section of a glassy carbon rod (diameter 3 mm; Tokai Carbon GC-20) embedded in Pyrex glass was used as a working electrode for the measurement of compounds in solution.

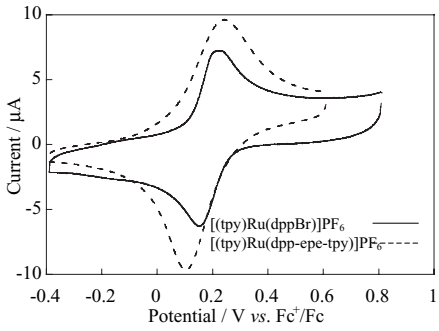


Figure 2.
Cyclic voltammograms of [(tpy)Ru(dppBr)]PF_6 and [(tpy)Ru(dpp-epe-tpy)]PF_6 at glassy carbon at a scan rate of 100 mVs^{-1} in 0.1 M Bu_4NClO_4-CH_2Cl_2.

Results and Discussion

UV-vis Spectra

UV-vis absorption spectra of Hepe-tpy, [(tpy)Ru(dppBr)]PF_6 and [(tpy)Ru(dpp-epe-tpy)]PF_6 in dichloromethane are shown in Fig. 1. The difference between the spectra indicates that the absorption band at 400 nm for [(tpy)Ru(dpp-epe-tpy)]PF_6 originated from the longer π-conjugation with a terpyridyl moiety through the phenylene-ethynylene bridge.

Cyclic Voltammetry of Ruthenium Complexes

Cyclic voltammetry of [(tpy)Ru(dppBr)]-PF_6 and [(tpy)Ru(dpp-epe-tpy)]PF_6 was carried out in 0.1 M Bu_4NClO_4-CH_2Cl_2, and the results are shown in Fig. 2. The cyclic voltammogram of [(tpy)Ru(dpp-epe-tpy)]PF_6 shows a reversible redox reaction of the Ru^{III}/Ru^{II} couple at $E^{0'} = 0.17$ V vs. ferrocenium/ferrocene (Fc^+/Fc), which was

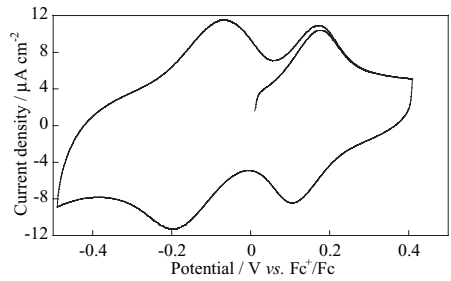


Figure 3.
A cyclic voltammogram of [**1Co1Ru**] film on Au at a scan rate of 100 mVs^{-1} in 0.1 M Bu_4NClO_4-CH_2Cl_2.

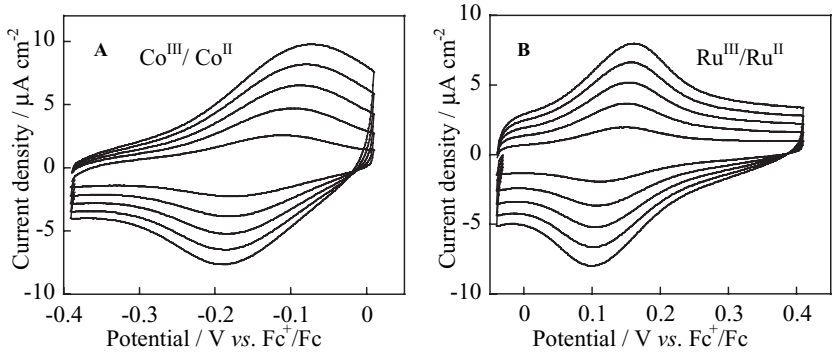


Figure 4.
Cyclic voltammograms of the [**1Co1Ru**] film on Au in the potential range of the Co^{III}/Co^{II} couple (A) and the Ru^{III}/Ru^{II} couple (B) in 0.1 M Bu_4NClO_4-CH_2Cl_2. The scan rates were 20, 40, 60, 80, 100 mVs^{-1} for the voltammograms from inside to outside.

slightly more negative than that of [(tpy)Ru(dppBr)]PF_6 ($E^{0'} = 0.19$ V).

Cyclic Voltammetry of Co-Ru Complex Wires on Au

A $Co(tpy)_2$-Ru(tpy)(dpp) complex wire, [**1Co1Ru**], was prepared at the Au/mica surface by immersion of a Au/mica plate in a chloroform solution of Au-connecting terpyridine ligand, $(tpyAB\text{-}S)_2$, in an aqueous solution of $CoCl_2$, and then in a dichloromethane solution of [(tpy)Ru(dpp-epe-tpy)]PF_6. Figure 3 displays a cyclic voltammogram of [**1Co1Ru**] in 0.1 M Bu_4NClO_4-CH_2Cl_2, showing a reversible peak of both Co^{III}/Co^{II} and Ru^{III}/Ru^{II} couples appearing at −0.15 V and 0.15 V *vs*. Fc^+/Fc, respectively. The proportionality of the peak current to the scan rate for both redox couples indicates that they are surface-confined redox species (see Figs. 4 and 5). The surface coverages of the electroactive cobalt and ruthenium complex sites in the film, Γ_{Co} and Γ_{Ru}, were estimated from the electric charge of the redox reaction. The values obtained are $\Gamma_{Co} = 8.7 \times 10^{-11}$ mol cm^{-2} and $\Gamma_{Ru} = 7.8 \times 10^{-11}$ mol cm^{-2}, indicating that almost all the cobalt complex units are connected to the ruthenium complex units.

It is interesting that the redox reaction of the ruthenium complex units is not

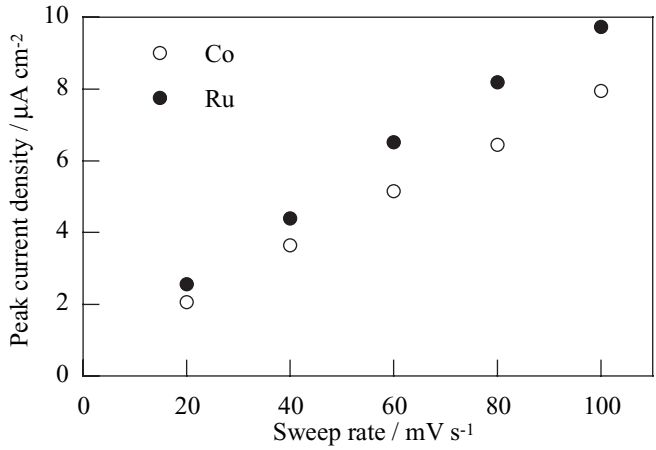


Figure 5.
Plots for the peak current density *vs*. the scan rate of [**1Co1Ru**] film.

inhibited by insertion of the cobalt complex unit between the electrode and the ruthenium complex moiety. This lack of inhibition implies that the complex wire is electronically conducting intrinsically, which has previously been observed in the case of complex wires made of azobenzene-bridged bis(terpyridine) ligands[1].

Conclusion

A new terpyridine ligand that has a ruthenium complex was synthesized and used to construct a redox-active hetero-metal complex wire, [**1Co1Ru**] fixed on the gold electrode surface by using the complexation of cobalt and terpyridine. The cyclic voltammogram of the film indicated that the ruthenium terpyridine complex was a surface-confined redox species. This hetero-metal complex molecular chain is expected to be used as an emission or photoelectric conversion device.

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