Electronic Supplementary Information

A Butadiyne-linked Diruthenium Molecular Wire Self-assembled on Gold Electrode Surface

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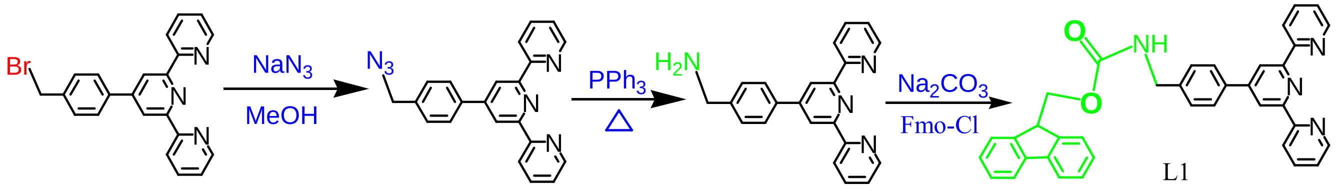
Experimental Section

Materials and Reagents. All operations were carried out under dry argon atmosphere by using Schlenk techniques at ambient temperature and vacuum-line system unless specified. The solvents were dried, distilled and degassed prior to use except those for spectroscopic measurements were of spectroscopic grade. $[Cp_2Fe](ClO_4)$,[1] 4'4'-p-Tolyl-2,2'':6',2''-terpyridine (Tp),[2] 4'-(p-bromomethyl-phenyl)-2,2':6',2''-terpyridine (Tp-Br),[2] and $[(Tp\text{-}Br)(PPh_3)_2RuCl](ClO_4)$[3] were prepared by the literature procedures. 9-Fluorenylmethyl chloroformate (Fmo-Cl), N,N'-dicyclohexylcarbodiimide (DCC), and 5-(1,2-dithiolan-3-yl)pentanoic acid etc were commercially available from Acros, Alfa Aesar, or TCI.

Physical Measurements. UV-vis absorption spectra were measured on a Perkin-Elmer Lambda 25 UV-vis spectrophotometer. Infrared spectra (IR) were recorded on a Magna 750 FT-IR spectrophotometer with KBr pellets. Elemental analyses (C, H, N) were carried out on a Perkin-Elmer model 240 C elemental analyzer. Electrospray mass spectrometry (ES-MS) was performed on a Finnigan LCQ mass spectrometer using dichloromethane methanol mixtures as mobile phases. The cyclic voltammograms (CV) were made with a potentiostat/galvanostat model 263A in dichloromethane solutions containing 0.1 M Bu_4NPF_6 as the supporting electrolyte. The CV was performed at a scan rate of 100 mV s^{-1}. Platinum and glassy graphite were used as the counter and working electrodes, respectively, and the potential was measured against a Ag/AgCl reference electrode.



Synthesis of the Ligand L1. To a 250 mL flask containing 75 mL of methanol were added 4'-(p-bromomethyl-phenyl)-2,2':6',2''-terpyridine (4.02 g, 10 mmol) and sodium azide (0.78 g, 12 mmol) with refluxing and stirring for 1 h to give a clear solution. Upon cooling, to the solution was added triphenylphosphine (2.90 g, 11 mmol) with stirring under reflux for 2 h. Upon removal of the solvents, to the flask were added dichloromethane (50 mL) and 10% aqueous solution of sodium carbonate (75 mL). The mixture was kept to a ice water bath and a dichloromethane (20 mL) solution of 9-fluorenylmethyl chloroformate (2.85 g, 11 mmol) was dropwise added. A precipitate formed and the stirring continued at ambient temperature for 1 d. Upon filtration, the white precipitate was sufficiently washed using water, ethanol, and diethyl ether, and then dried in vacuo. Yield: 85%. mp: 153-156°C. Anal. Calcd for $C_{37}H_{28}N_4O_2{\cdot}H_2O$: C, 76.80; H, 5.23; N, 9.68. Found: C, 77.43; H, 5.17; N, 9.94. ESI-MS (%): 561 (100) $[M+1]^+$. IR (KBr, cm^{-1}): 3315m (NH), 1698s (C=O). The ^1H NMR was not measured because it is insoluble in common organic solvents.

Preparation of $[Ru(L1)(PPh_3)_2Cl](ClO_4)$ ($[1](ClO_4)$). To a Schlenk flask containing 150 mL of benzene were added ligand L1 (1.12 g, 2 mmol) and $Ru(PPh_3)_3Cl_2$ (1.92 g, 2 mmol) and the mixture was heated under reflux for 2 h with the color change from brown to purple. After the solvent removed, to the purple residue were added triphenylphosphine (1.58 g, 6 mmol) and 150 mL of ethanol-acetone (v/v=2:1). After the solution was kept in dark with stirring for 8 h, an excess ammonium perchlorate (0.3 g, 2.56 mmol) was added. The acetone was then removed by evaporation and the brown precipitate was taken by filtration, washed sufficiently with water, ethanol, and diethyl ether. The crude product was dissolved in dichloromethane and purified by chromatography on a silica gel column. Red-brown band was collected using dichloromethane-acetone (v/v=8:1) as eluent. Yield: 65%. Anal. Calcd for $C_{73}H_{58}Cl_2N_4O_6P_2Ru{\cdot}H_2O$: C, 65.47; H, 4.52; N, 4.18. Found: C, 65.62; H, 4.47; N, 4.13. ESI-MS [*m*/*z* (%)]: 1222 (100) $[M\text{-}ClO_4]^+$. ^1H NMR (CD_3CN, ppm): 9.21(d, 2H, *J*=5.2Hz), 7.86(t, 4H, *J*=8.6Hz), 7.73–7.66(m, 6H), 7.60(s, 2H), 7.50-7.44(m, 4H), 7.38(t, 2H, *J*=7.2Hz), 7.27–7.22(m, 20H), 7.12–7.08(m, 12H), 6.30(t, 1H, *J*=6.0Hz), 4.45(d, 2H, *J*=6.4Hz), 4.40(d, 2H, *J*=6.0Hz), 4.29(t, 1H, *J*=6.8Hz). ^{31}P NMR (CD_3CN, ppm): 19.62 (s). IR (KBr, cm^{-1}): 3422w (N-H)，1718m (C=O)，1089s (ClO_4), 697s (P-C). UV-vis (CH_2Cl_2): λ/nm ($\varepsilon/dm^3mol^{-1}cm^{-1}$) = 268 (68700), 301 (38000), 315 (33800), 495(6460).

Preparation of $[\{Ru(L1)(PPh_3)_2\}_2(C{\equiv}CC{\equiv}C)](ClO_4)_2$ ($[2](ClO_4)_2$). To a 50 mL of microwave flask were added **1** (200 mg, 0.151 mmol), 1,4-bis(trimethylsilyl)-1,3-butadiyne (14.7 mg, 0.076 mmol), potassium fluoride (16.8 mg, 0.3 mmol), and methanol (20 mL). The microwave reaction was performed in a Biotage Initiator Microwave Synthesizer at 100°C for 20 min. The solvent was removed and the green residue was dissolved in dichloromethane. The solution was chromatographed on a silica gel column to collect the green band using dichloromethane-acetone (v/v=5:1) as eluent. Yield: 30%. ESI-MS [m/z (%)]: 1211.5 (100) $[M{-}2ClO_4]^{2+}$. Anal. Calcd for $C_{150}H_{116}Cl_2N_8O_{12}P_4Ru_2{\cdot}CH_2Cl_2{\cdot}3(CH_3COCH_3)$: C, 66.76; H, 4.76; N, 3.89. Found: C, 66.38; H, 5.37; N, 3.43. ^{1}H NMR (CD_3CN, ppm): 9.01 (d, 4H, *J*=5.2 Hz), 7.91–7.87 (m, 8H), 7.77–7.69 (m, 16H), 7.66-7.60(m, 20H), 7.53-7.45 (m, 8H), 7.41-7.38 (m, 8H), 7.16-7.08 (m, 20H), 6.93-6.89 (m, 20H), 6.33 (t, 2H, *J*=6.0 Hz), 4.46(d, 4H, *J*=6.8Hz), 4.42 (d, 4H, *J*=6.4Hz), 4.30 (t, 2H, *J*=6.4Hz). IR (KBr, cm^{-1}): 3422w (N-H), 1967w (C≡C), 1708m (C=O), 1088s (ClO_4), 697s (P–C). UV-vis (CH_2Cl_2): λ/nm (ε/dm^{3}mol^{-1}cm^{-1}) = 267 (133000), 300 (94800), 315 (79600), 412(17700), 641(12600).

Preparation of $[\{Ru(L1)(PPh_3)_2\}_2(C{\equiv}CC{\equiv}C)](ClO_4)_3$ ([2a]$(ClO_4)_3$). To a dichloromethane (20 mL) solution of [**2**]$^{2+}$ (131 mg, 0.05 mmol) was added $(Cp_2Fe)(ClO_4)$ (14.3 mg, 0.05 mmol) with stirring at ambient temperature for 2 h. The solution was concentrated to precipitate the green product by addition of diethyl ether. The crude product was sufficiently washed with diethyl ether to remove the produced Cp_2Fe. Recrystallization in dichloromethane solution by diffusion of diethyl ether afforded the pure product. Yield: 80%. ESI-MS [m/z (%)]: 806.9 (100) $[M{-}3ClO_4]^{3+}$. IR (KBr, cm^{-1}): 3422m (N–H), 1855w (C≡C), 1715m (C=O), 1091s (ClO_4), 698m (P–C). UV-vis (CH_2Cl_2): λ/nm (ε/dm^{3}mol^{-1}cm^{-1}) = 267 (127000), 301 (85500), 420(13700), 602(7050), 820(9830), 1011(25100).

Preparation of $[\{Ru(L2)(PPh_3)_2\}_2(C{\equiv}CC{\equiv}C)](ClO_4)_2$ ([3]$(ClO_4)_2$). To 10 mL of DMF- piperazine (v/v = 4:1) was added [**2**]$^{2+}$ (100 mg) with stirring at ambient temperature for 4 h. Upon addition of 100 mL of water, the solution was extracted thrice with 100 mL of dichloromethane. The extracted solution was dried using $MgSO_4$ for 1 h, and then concentrated. The product was isolated by diffusion of diethyl ether into the dichloromethane solution, and dried using P_2O_5 for 1 d. This compound was not characterized because of its instability and used directly to prepare the next product **4**.

Preparation of [{Ru(L3)(PPh$_3$)$_2$}$_2$(C≡CC≡C)](ClO$_4$)$_2$ ([4](ClO$_4$)$_2$). To a dichloromethane (20 mL) solution of **3** were added 5-(1,2-dithiolan-3-yl)pentanoic acid (20 mg) and N,N'-dicyclohexylcarbodiimide (20 mg) with stirring at ambient temperature for 1 d. After taken by filtration, the solution was concentrated and the product was purified by chromatography on a silica gel column. The main band (red brown) was collected using dichloromethane-acetone (v/v = 3:1) as eluent to give a red-brown product. Yield: 50%. Anal. Calcd for $C_{136}H_{120}Cl_2N_8O_{10}P_4Ru_2S_4\cdot CH_2Cl_2\cdot 3H_2O$: C, 61.16; H, 4.79; N, 4.16; Found: C, 61.45; H, 5.32; N, 3.72. ESI-MS [m/z (%)]: 1175.7 (100) $[M–2ClO_4]^{2+}$. ^{1}H NMR (CD$_3$CN, ppm): 9.00 (d, 4H, *J*=5.6 Hz), 7.89 (d, 4H, *J*=8.0 Hz), 7.77-7.69 (m, 10H), 7.66-7.60 (m, 18H), 7.54 (d, 4H, *J*=8.0 Hz), 7.49-7.38 (m, 8H), 7.28-7.22 (m, 4H), 7.20-7.07 (m, 20H), 6.93-6.89 (m, 18H), 7.01 (t, 2H, *J*=6.0 Hz), 4.48 (d, 2H, J=6.4Hz), 3.70-3.61 (m, 2H), 3.23-3.08 (m, 4H), 2.52-2.45 (m, 2H), 2.28 (t, 4H, *J*=7.2 Hz), 1.92-1.87 (m, 2H), 1.71-1.60 (m, 8H), 1.52-1.44 (m, 4H). IR (KBr, cm^{-1}): 3419m (N–H), 1992m (C≡C), 1637m (C=O), 1090s (ClO$_4$), 698m (P–C). UV-vis (CH$_2$Cl$_2$): λ/nm (ε/dm^{3}mol^{-1}cm^{-1}) = 268 (97800), 294 (79600), 314(74900), 640(9800).

Preparation of Self-Assembled Monolayer (SAM) and Physical Measurements. An Au(111) electrode was immersed into a CH$_2$Cl$_2$ solution of [**4**](ClO$_4$)$_2$ (1.0 mM) for 1 d. It was taken out and rinsed thoroughly with CH$_2$Cl$_2$ and dried in an argon atmosphere. The gold electrode modified with the monolayer of [**4**](ClO$_4$)$_2$ was used as a working electrode for cyclic voltammetry measurements in a 0.1 M *n*-Bu$_4$NPF$_6$ (TBAP)-CH$_2$Cl$_2$ solution.

A thin gold film was chemically deposited on the flat reflecting side of a hemicylindrical Si prism as the substrate.[4] Prior to use, the gold film electrode was electrochemically cleaned and rinsed by Mill-Q water. The gold substrate was dipped for 24h in a 1.0 mM CH$_2$Cl$_2$ solution of [**4**](ClO$_4$)$_2$ for self-assembly. After being thoroughly rinsed with CH$_2$Cl$_2$ and dried by Ar gas, the gold electrode was mounted in a spectroelectrochemical cell with the Krestchmann ATR configuration for *in situ* IR measurement.

The reaction process was monitored by means of *in situ* IR measurement with the Kretschmann attenuated total reflection (ATR) configuration.[5] The use of an ATR configuration for IR measurement facilitates *in situ* monitoring of the electrode process owing to the fact that it is free from the mass transport problem. IR spectra at 4 cm^{-1} resolution were recorded on a Bio-RadFTS 60 A/896 FT-IR spectrometer equipped with a liquid nitrogencooled MCT detector. All the IR spectra are shown in absorbance units, defined as $A = -\log I/I_0$, where I and I_0 represent the IR absorption intensities of the sample state and background state, respectively. The integration time of the IR spectra in different experiments is given in the Fig. captions. A homemade single-reflection accessory (incident angle of 70^o) and a Harrick grazing angle (ca.70^o) reflection accessory were used for *in situ* and *ex situ* IR measurements, respectively. The spectroelectrochemical cells were of a three-electrode design.[6] The working electrode was the gold electrode modified with the monolayer of [**4**]$(ClO_4)_2$. The counter electrode was a Pt foil and the reference electrode was a Ag/AgCl (saturated KCl) electrode. A solution of CH_2Cl_2 with *n*-Bu_4NPF_6 (0.1M) was employed as the electrolyte. A potentiostat (model 263 A, EG&G PARC) was used to control the electrode potential. Prior to the electrochemical measurement, the electrolyte solution was deaerated with Ar gas for about 30 min.

References

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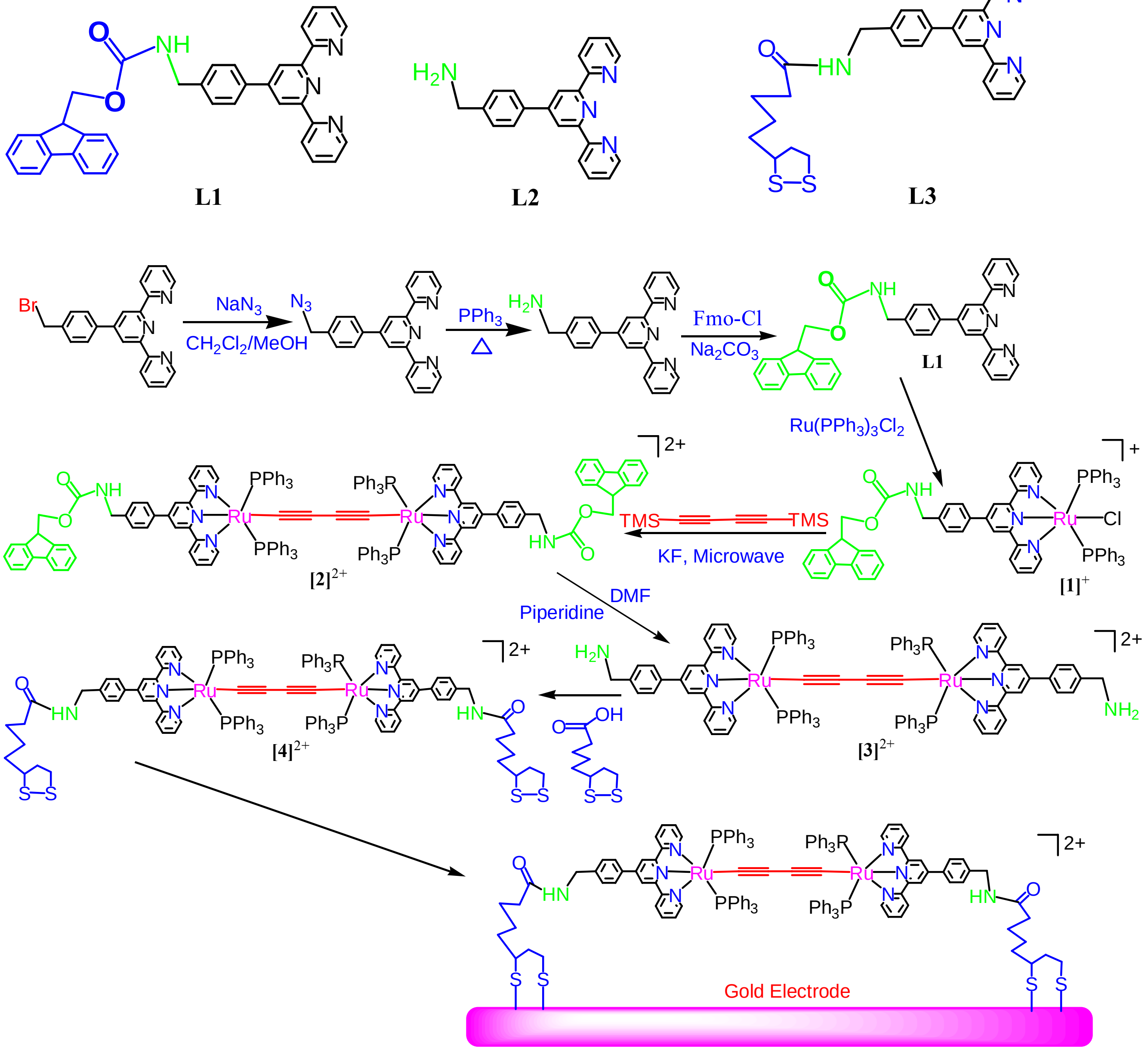

Scheme S1. Synthetic routes to the ligands and complexes [**1**]$^+$–[**4**]$^{2+}$.

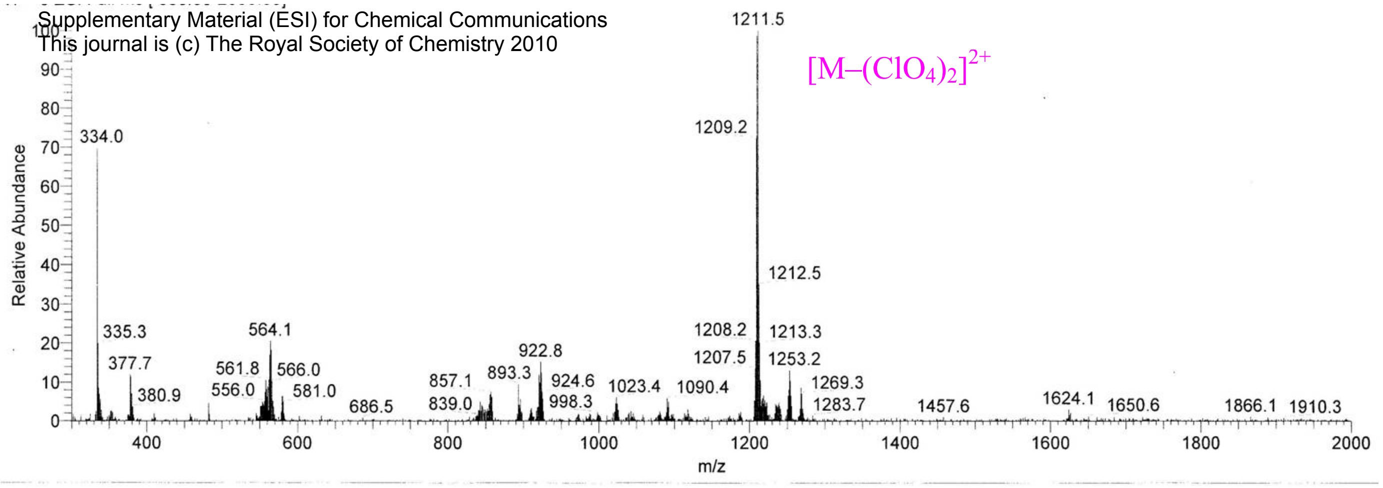

Fig. S1. ESI-MS of **2** in CH_3OH-CH_2Cl_2 mobile phase.

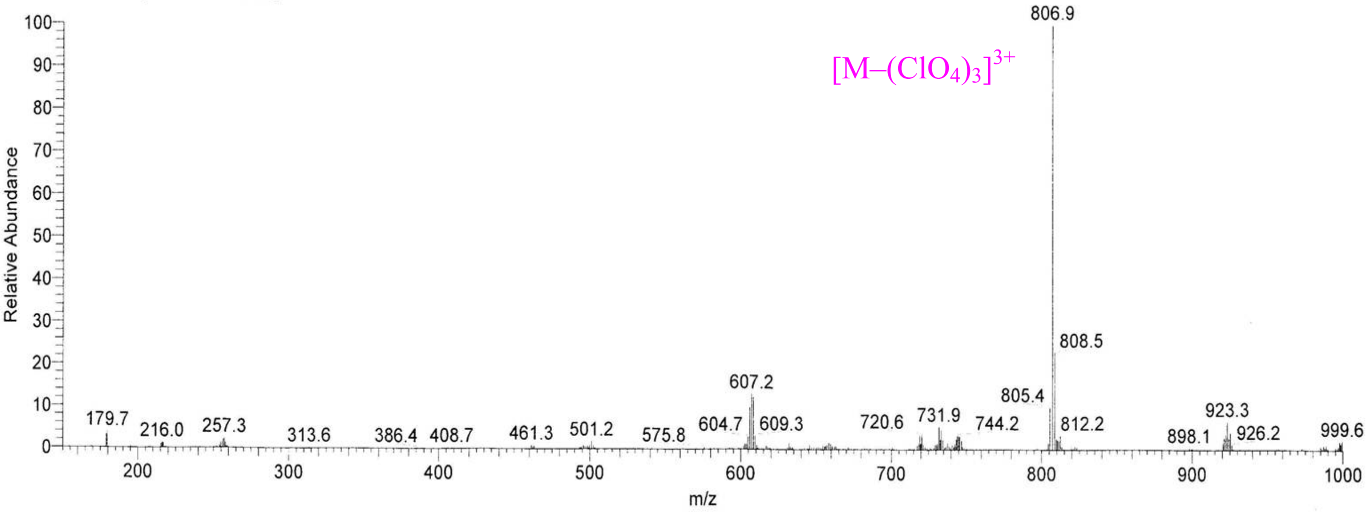

Fig. S2. ESI-MS of **2a** in CH_3OH-CH_2Cl_2 mobile phase.

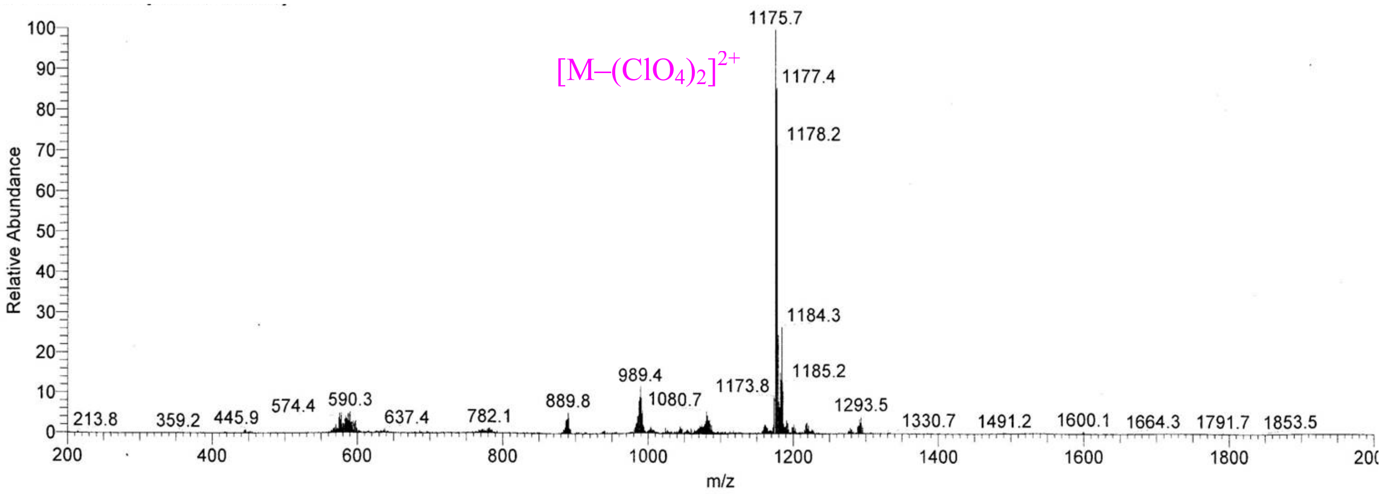

Fig. S3. ESI-MS of **4** in CH_3OH-CH_2Cl_2 mobile phase.

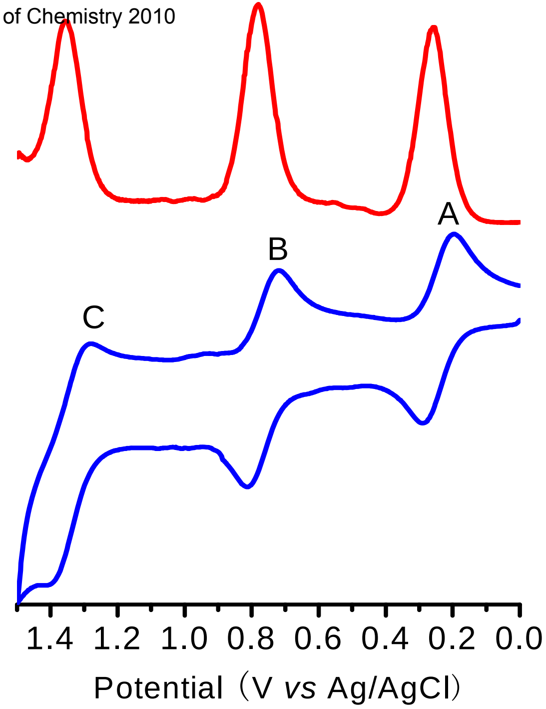

Fig. S4. Plots of cyclic and differential pulse voltammograms of **2** in 0.1 M CH_2Cl_2-TBAP solution. The scan rate is 100 mV s^{-1}.

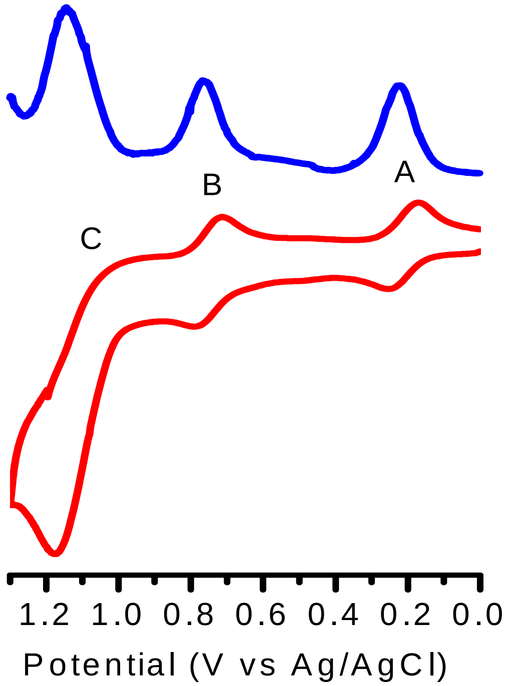

Fig. S5. Plots of cyclic and differential pulse voltammograms of **4** in 0.1 M CH_2Cl_2-TBAP solution. The scan rate is 100 mV s^{-1}.

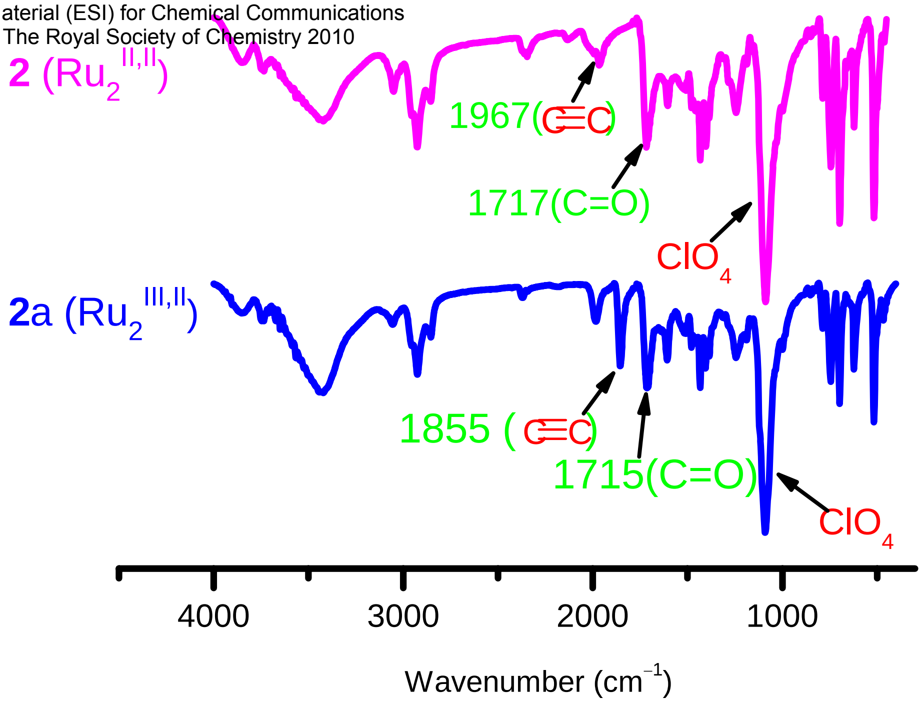

Fig. S6. Infrared spectra of Ru$_2^{II,II}$ complex [**2**]$^{2+}$ and Ru$_2^{III,II}$ species [**2a**]$^{3+}$ in KBr pellet.

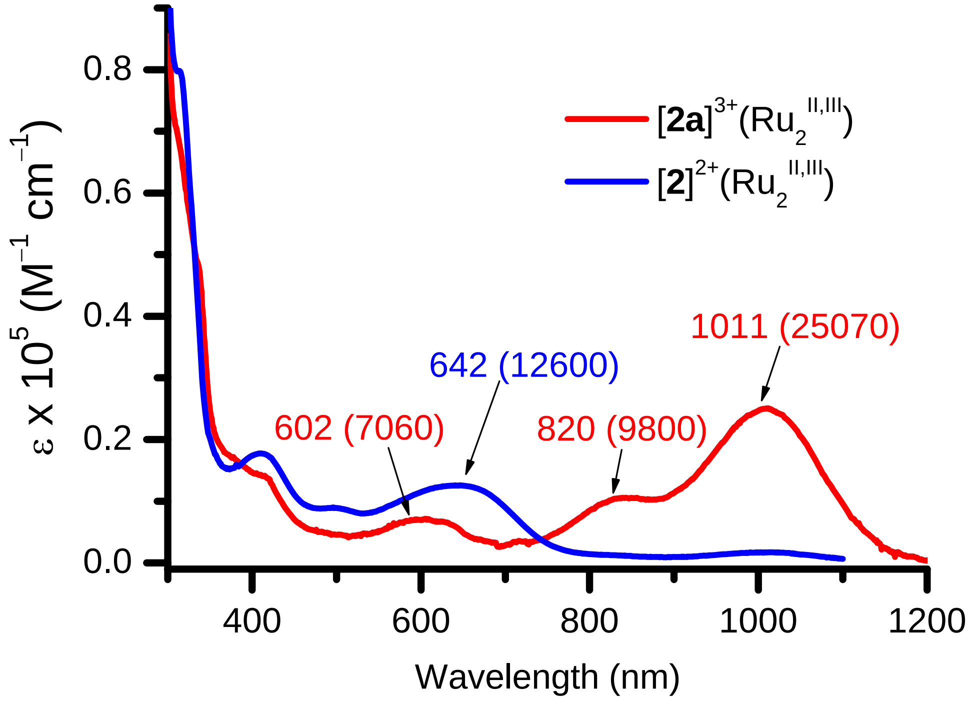

Fig. S7. UV-Vis-NIR spectra of Ru$_2^{II,II}$ complex [**2**]$^{2+}$ and Ru$_2^{III,II}$ species [**2a**]$^{3+}$ in dichloromethane solutions.

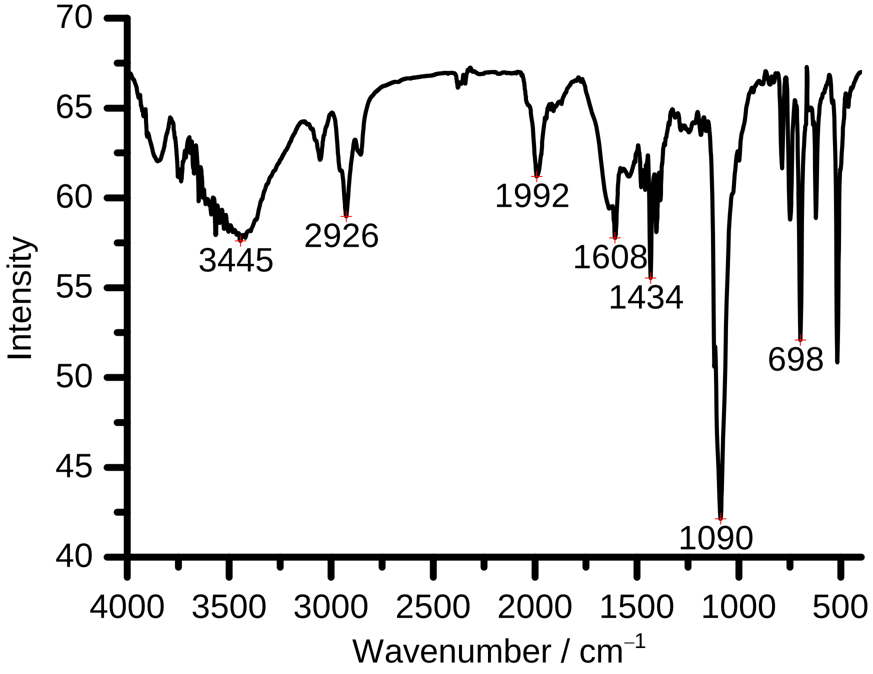

Fig. S8. IR transmission spectrum of [**4**]$^{2+}$ in a KBr matrix.