

Surface-Enhanced Raman Scattering of Ruthenium (II) Complex Adsorbed on Silver Colloid

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Complexes of ruthenium (II) with 2,2'-bipyridine (bpy) and related ligands have been studied widely because of their excited-state redox properties and the potential application of these compounds in areas as diverse as solar energy conservation,¹⁻⁴ artificial photosynthesis,⁵ tests of theories of photophysics of electron-transfer reactions,⁶⁻⁸ and as candidates for components in molecular devices.⁹ A number of recent studies have demonstrated the utility of surface-enhanced Raman scattering (SERS) for investigating the structure of adsorbed molecules and characterizing the interactions between the molecules and metal surface.¹⁰⁻¹⁵ Resonance Raman (RR) and SERS spectra of ruthenium complexes containing π -conjugated ligands have received considerable interest.¹⁶⁻²⁰ Resonance Raman spectroscopy of ruthenium(II) polypyridine complexes has played an important role in elucidating both ground- and excited-state properties of these molecules. Vibrational frequencies yield the information about the ground-state geometries of the coordinated ligands, whereas intensities can be indicative of the specific normal modes that are most efficient in coupling between the ground and excited states during absorption and emission, if one can assume that the emissive and absorptive excited states are similar. We have also reported that SERS and SERRS spectra of ruthenium (II) complexes adsorbed on silver colloid showed substantial enhancement of Raman cross-section and luminescence was strongly quenched.²¹

The purpose of this study is to investigate the molecular structure and surface interaction of ruthenium (II) complex adsorbed on silver colloid by means of RR and SERS. A particular attention is paid on the synthesis and characterization of ruthenium (II) complexes containing BIK, [bis(1-methylimidazol-2-yl)ketone] as a polypyridine ligand, because mononuclear ruthenium (II) complexes such as *cis*-[Ru(bpy)₂L], (bpy=2,2'-bipyridine, L=bidentate ligand) are of a great importance owing to their potential application as catalysts for the photodecomposition of water.^{22,23}

Experimental Section

Samples. RuCl₃·3H₂O, 2,2'-bipyridine (bpy), 1-methylimidazole, sodium borohydride and silver nitrate were obtained from Aldrich Chemical Co. and used without further purification.

Preparation of [Ru(bpy)₂(BIK)](PF₆)₂. The bidentate ketone [bis(1-methylimidazol-2-yl)ketone, BIK] (Figure 1)

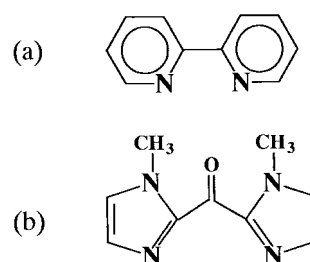


Figure 1. Molecular structures of 2,2'-bipyridine(bpy) ligand (a) and [Bis(1-methylimidazol-2-yl) ketone] (BIK) ligand.

was prepared following the method of Elgafi and coworkers.²⁴ The complex *cis*-[Ru(bpy)₂Cl₂] was prepared following the literature procedures.²⁵ Distilled water used in this work was obtained by using a Barnsted water purification system. The complex *cis*-[Ru(bpy)₂Cl₂] (0.5 mmol) was dissolved in water (30 mL) after stirring and heating at 75 °C on a water bath for 30 min. BIK (0.5 mmol) was added and heating continued for an hour to give a reddish solution. The product was precipitated by addition of NH₄PF₆ (2.5 mmol), filtered and washed with cold water, diethyl ether and then dried in vacuum.

Analysis of Elements of [Ru(bpy)₂(BIK)](PF₆)₂. Calc.: C, 37.97%; H, 2.87%; N, 12.05%. Found: C, 37.85%; H, 2.91%; N, 12.11%.

Preparation of Colloid. Silver colloid used as active substrates of SERS in this study was prepared by the chemical reduction method similar to that reported by Creighton *et al.*²⁶ A solution of 150 mL of sodium borohydride (2 × 10⁻³ M) was mixed with a solution of 50 mL of silver nitrate (5 × 10⁻³ M) with strong stirring in an ice-cold bath, yielding greenish yellow silver colloid with an absorption maximum of 395 nm.

Spectrometers. All Raman spectra were obtained using a Raman spectrometer equipped with a SPEX 1403 scanning double monochromator and an RCA C31034 PMT tube detector. Coherent Innova 90-5 argon ion laser was used as the light source. UV-Vis spectrum was obtained in quartz cell by using a Shimadzu UV-2101 PC instrument.

Results and Discussion

Figure 2 A and B show the 488.0 and 514.5 nm-excited Raman spectra of acetonitrile solution of [Ru(bpy)₂(BIK)]

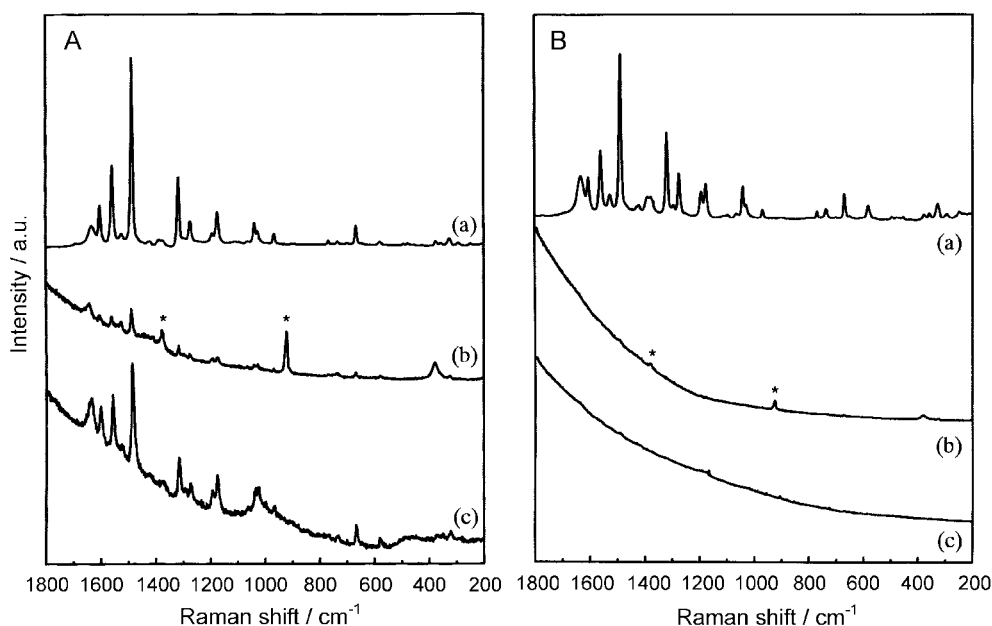


Figure 2. (A) 488.0 nm-excited Raman spectra of acetonitrile solution of $[\text{Ru}(\text{bpy})_2(\text{BIK})](\text{PF}_6)_2$ (1×10^{-3} M) with (a) and without (b) silver colloid and solid of $[\text{Ru}(\text{bpy})_2(\text{BIK})](\text{PF}_6)_2$ itself (c). Bands with an asterisk are due to solvent (acetonitrile). (B) 514.5 nm-excited Raman spectra of acetonitrile solution of $[\text{Ru}(\text{bpy})_2(\text{BIK})](\text{PF}_6)_2$ (1×10^{-3} M) with (a) and without (b) silver colloid and solid of $[\text{Ru}(\text{bpy})_2(\text{BIK})](\text{PF}_6)_2$ itself (c). Bands with an asterisk are due to solvent (acetonitrile).

$(\text{PF}_6)_2$ (1×10^{-3} M) with (a) and without (b) silver colloid and solid of ruthenium (II) complex itself (c), respectively. The 488.0 and 514.5 nm-excited Raman spectra of ruthenium (II) complex adsorbed on silver colloid show very intense bands with high signal-to-noise ratio owing to surface enhancement effect as shown in Figure 2A and B. Particularly striking is that the 488.0 nm-excited Raman spectrum of ruthenium (II) complex solution itself is markedly different from its 514.5 nm-excited Raman spectrum. It is not possible to record the 514.5 nm-excited Raman spectrum of ruthenium (II) complex solution due to strong fluorescence while its 488 nm-excited Raman spectrum shows the resonance effect by contribution of MLCT [metal-to-ligand charge transfer, ruthenium (d) \rightarrow bpy (π^*)] transition, which

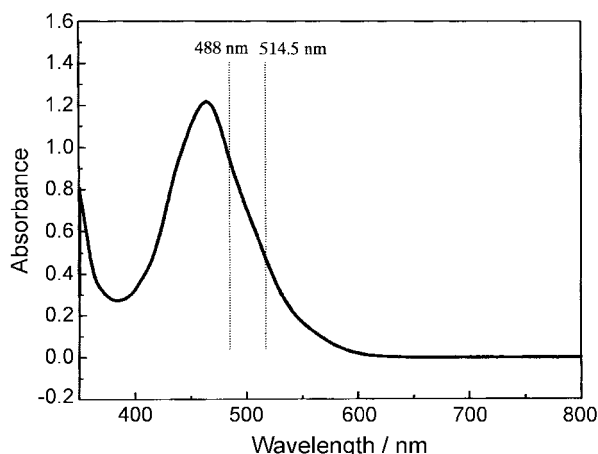


Figure 3. UV-Vis absorption spectrum of acetonitrile solution of $[\text{Ru}(\text{bpy})_2(\text{BIK})](\text{PF}_6)_2$.

is shown a band at 464 nm in UV-vis absorption spectrum in Figure 3.

The vibrational mode assignments in SERS spectra of ruthenium (II) complex were made by comparison with published data.^{20,27} Bands at 1603 and 1559 cm^{-1} are assigned skeletal stretching modes of the pyridine moieties. Of particular note in Figure 2A and B is that the vibrational bands near 1300-1500 cm^{-1} regions are stronger than those of in other regions in SERS spectra. It is reflected that C-C and C-N bands are affected mostly by the electron transfer from metal d-orbital to pi system of bipyridine ligand. The intense band at 1488 cm^{-1} corresponds to the C-C stretching containing C-H bending. A band at 1317 cm^{-1} represents C-C inter-ring stretching vibration with a large contribution of C-H bending.²¹ The band at 1274 cm^{-1} due to a combination of ring deformation and C-H bending and bands at 1194 and 1175 cm^{-1} due to both C-N and C-C stretching are also shown. Bands at 768, 735, and 667 cm^{-1} are assigned to large displacement of the nitrogen atom. The stretching vibration band of Ru-N is shown at 325 cm^{-1} .

It is also of note in Figure 2A and B that the relative intensity of SERS spectra of ruthenium complex obtained at between 488 and 514.5 nm excitation is different, suggesting that its surfaced-enhanced (resonance) Raman scattering [SER(R)S] spectrum is dominated by the contribution of bipyridine ligand whose MLCT transition is in near resonance with the 488 nm exciting radiation. In order to investigate the contribution of two kinds of ligands shown in Figure 2 to resonance effect, we have measured 488 nm-excited SERS spectra of two kinds of ligands (Figure 4). It reveals that the contribution of bipyridine ligand to resonance effect of Raman spectrum is significant. As shown in

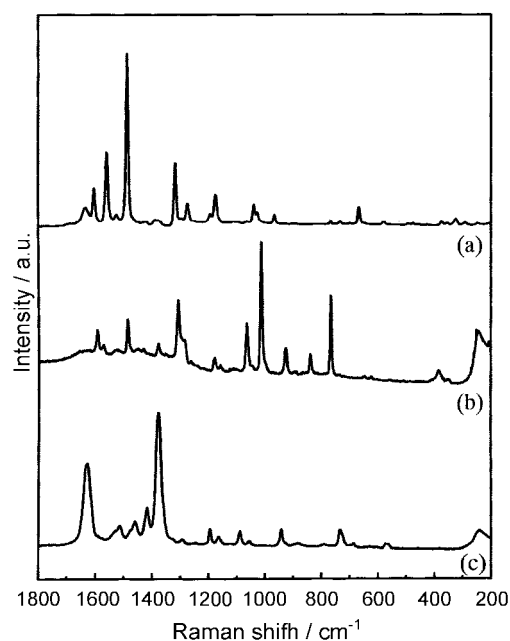


Figure 4. 488 nm-excited SERS spectra of $[\text{Ru}(\text{bpy})_2(\text{BIK})](\text{PF}_6)_2$ (a), bipyridine ligand (b), and BIK ligand (c) on silver colloid.

Figure 2A. SER(R)S spectrum of ruthenium complex is similar with the resonance Raman (RR) spectrum despite of the fact that RR spectrum is of poor quality because of the luminescence of the compound and show only very small frequency shifts and no change in relative intensities, it suggests that molecules may do not react chemically with the silver colloid. The lowest concentration at which the SERS signals were observed is 10^{-12} M.

Conclusion

Raman spectra of ruthenium (II) complex adsorbed on silver colloid are shown the strong surface enhancement effect even for the 10^{-12} M solution and resonance effect at which the excitation wavelength is close to the MLCT $[\text{Ru}(\text{d}) \rightarrow \text{bpy}(\pi^*)]$ transition absorption band. As shown in SER(R)S spectra, the fluorescence background is reduced owing to the surface interaction between ruthenium (II) complex and silver colloid. From the comparison between RR and SERS spectra of ruthenium (II) complex, SERS spectrum shows the Raman bands whose frequencies are very close to those of RR spectrum. Thus, it seems very likely that the electromagnetic enhancement mechanism is dominant for the silver colloid system.

The predominant bands in SERS spectra of $[\text{Ru}(\text{bpy})_2(\text{BIK})](\text{PF}_6)_2$ may be attributed by the contribution of bipyridine ligand whose MLCT transition is in near resonance with the 488 nm exciting radiation. Recalling the literature

data in Ru(II) complexes,^{21,27} it suggest that the election is transferred from metal (Ru) to the ligand (bpy) ligand, such that $[\text{Ru}(\text{bpy})_2(\text{BIK})]^{2+} \rightarrow [\text{Ru}^{\text{III}}(\text{bpy})_2(\text{BIK})]^{2+}$.

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