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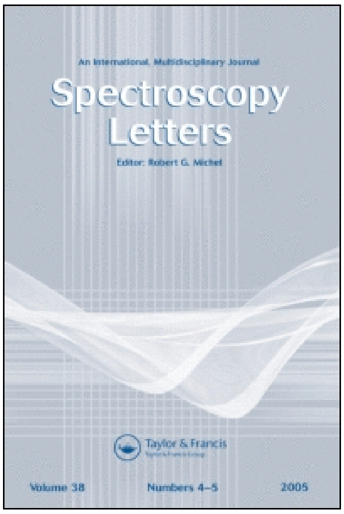

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Adsorption of Bipyridine Compounds on Gold Nanoparticle Surfaces Investigated by UV-Vis Absorbance Spectroscopy and Surface Enhanced Raman Scattering

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Abstract: Adsorption behaviors of 2,2′-bipyridine (2,2′-BiPy), 2,4′-bipyridine (2,4′-BiPy), and 4,4′-bipyridine (4,4′-BiPy) on gold nanoparticle surfaces have been comparatively investigated by means of UV-vis absorbance spectroscopy and surface-enhanced Raman scattering (SERS). The three bipyridine compounds are assumed to have a standing geometry on Au surfaces as indicated from several spectral features and relative vibrational intensity factors on the basis of the electromagnetic (EM) selection rule. 2,4′-BiPy appears to adsorb on Au surfaces via the 4-pyridyl nitrogen atom as suggested from the stronger enhancement of the vibrational bands ascribed to the 4-pyridyl ring. The SERS intensities for the three bipyridine compounds on Au could be ascribed to both the electromagnetic (EM) and charge transfer (CT) enhancement mechanism. The charge transfer is assumed to be dissimilar for 2,2′-BiPy, 2,4′-BiPy, and 4,4′-BiPy due to their different positions of the nitrogen atoms as indicated from the disparate ν_{8a} band enhancements upon adsorption on surfaces.

Keywords: Bipyridine, Au, nanoparticles, adsorption, SERS

INTRODUCTION

Adsorption of bipyridine compounds on metal surfaces have attracted much attention due to its potential application in many areas such as energy

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storage,[1] photocatalytic systems,[2] dye-sensitized solar cells,[3] molecular electronics,[4] and electroluminescent devices.[5] An understanding of physicochemical properties in self-assembled monolayers prepared by bipyridine compounds on metal substrates should be important in designing a novel nanoscale molecular electronic device.

Infrared and Raman spectroscopic tools have been applied to investigate the adsorption behaviors of bipyridine compounds on metal surfaces.[6–18] 2,2′-Bipyridine (2,2′-BiPy) is found to have a *trans* conformation in its crystalline and solution phase, whereas it appears to have a *cis* conformation upon adsorption on metal substrates.[10,11] 4,4′-Bipyridine (4,4′-BiPy) is assumed to have a standing geometry on Au surfaces.[16,18] Complexes of 2,4′-bipyridine (2,4′-BiPy) are characterized to coordinate to the metal Co and Cd centers via its 4-pyridyl nitrogen atoms.[19]

Surface-enhanced Raman scattering (SERS) has been one of the most sensitive techniques to monitor the adsorbates on metal substrates at the submonolayer coverage limit despite the equivocal selection rule and limited applicability to a few metals.[20] To date, only qualitative arguments concerning molecular orientation have been offered for data obtained via SERS, since it has been difficult to model real surfaces due to the fact that both a long range electromagnetic (EM) effect and a short range chemical effect are assumed to simultaneously operate for the overall enhancement.[21–23]

On the basis of the electromagnetic (EM) surface selection rules,[22,23] the interfacial structures of aromatic adsorbates on silver and gold nanoparticles could be explained in a more quantitative way.[24,25] An additional contribution to the SERS phenomenon is the charge transfer (CT) mechanism considered as analogous to a resonance Raman process, although it strongly depends on the nature of the metal-adsorbate system without general rules.[26–28]

Recently a SERS study of 4,4′-BiPy on gold nanoparticle surfaces indicates that both EM and CT mechanisms should contribute the enhancements upon adsorption.[18] To better understand the adsorption characteristics and the enhancement mechanisms of self-assembled monolayers based on bipyridines, SERS of 2,2′-BiPy, 2,4′-BiPy, and 4,4′-BiPy was performed on Au nanoparticle surfaces. Although a number of Raman spectra of 2,2′-BiPy and 4,4′-BiPy are previously reported,[6–17] a comparative SERS study of the bipyridine compounds has not been performed yet. To the best of the author's knowledge, this is the first SERS study of 2,4′-BiPy on Au surfaces with a comparison of 2,2′-BiPy and 4,4′-BiPy.

EXPERIMENTAL

The citrate-stabilized gold nanoparticle was synthesized by following the recipes in the literature.[29] A 133.5 mg portion of $KAuCl_4$ (from Aldrich) was initially dissolved in 250 ml of water, and the solution was brought to boil. A solution of 1% sodium citrate (25 ml) was then added to the $KAuCl_4$ solution under vigorous stirring, and boiling was continued for ca. 20 min. The resulting Au nanoparticle solution was stable for several weeks. 2,2′-BiPy was purchased from Sigma Aldrich. 2,4′-BiPy, and 4,4′-BiPy were purchased from Tokyo Kasei. All the chemicals otherwise specified were reagent-grade, and triply distilled water with resistivity greater than $18.0\,M\Omega\cdot cm$ was used in making aqueous solutions.

Raman spectra were obtained using a Renishaw Raman confocal system model 1000 spectrometer equipped with an integral microscope (Leica DM LM). The 632.8 nm from a 35 mW air-cooled HeNe laser (Melles Griot Model 25 LHP 928) with the plasma line rejection filter were used as the excitation sources for the Au SERS experiments. ~0.1 M aqueous solution of 2,4′-BiPy and ethanolic solutions of the 2,2′-BiPy and 4,4′-BiPy were added dropwise to 0.1 ~ 1 ml of Au nanoparticle solution to a final concentration of $\sim 10^{-3}$ M using a micropipet. The concentrations of 2,2′-BiPy, 2,4′-BiPy and 4,4′-BiPy at $\sim 10^{-3}$ M in all the SERS spectra were higher than those required for its monolayer coverage. The purple gold nanoparticles became bluish green by the addition of the bipyridine solution. UV-vis absorbance spectra were checked by a Shimadzu UV-3101 PC spectrophotometer.

RESULTS AND DISCUSSION

The geometry of aromatic compounds on metal surfaces has been inferred from the presence of the ν_2 band in the previous SERS studies.[24,25] The ring CH stretching ν_2 band was clearly observed at $\sim 3060\,cm^{-1}$ in the Au SERS spectra for the three bipyridine compounds under our experimental conditions. Plausible orientations of the three bipyridine compounds are depicted in Fig. 1.

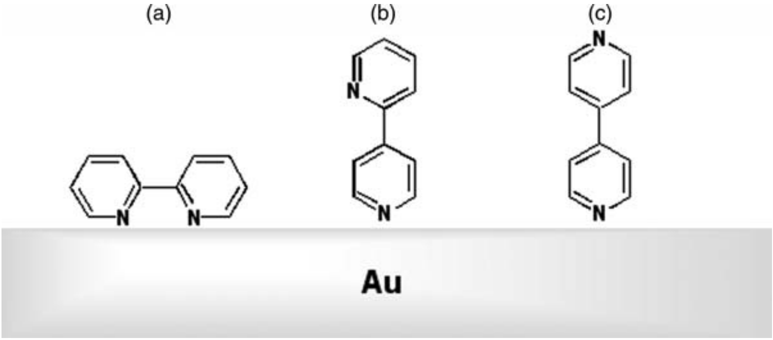

Figure 1. Plausible orientations of (a) 2,2′-BiPy, (b) 2,4′-BiPy, and (c) 4,4′-BiPy on gold. The three bipyridine compounds assumed to be protonated on Au nanoparticle surfaces due to the low pH condition are not depicted in the picture.

Fig. 2a shows the ordinary Raman (OR) spectrum of 2,2′-BiPy in the solid state. 2,2′-BiPy is found to have a *cis* configuration on Au as consistent with the previous reports.[10,11] It is noteworthy that the ν_{8a} band of 2,2′- BiPy appeared to be least enhanced. It was previously reported that the intensity of the ν_{8a} band of 2,2′- BiPy varied depending on the pH conditions.[7] At a neutral pH similar to the present experimental condition, the ν_{8a} band intensity was observed to be quite weak as consistent with our data. The ordinary Raman (OR) in the solid state and the Au nanoparticle SERS spectra of 4,4′-BiPy are shown in Figs. 2c and d, respectively. It is noteworthy that the ν_{8a} mode is found to be most enhanced for 4,4′-BiPy,

Fig. 2e shows the ordinary Raman (OR) spectrum of 2,4′-BiPy in the solid state. Since it is not absolutely certain whether the pyridine rings of 2,4′-BiPy should twist with respect to one another without lying on the same plane, the major bands associated with the ring vibrational modes can be divided into two symmetry species assuming C_2 symmetry[30] in the OR spectrum. Their peak positions are listed in Table 1 along with the appropriate vibrational assignments. The Au nanoparticle SERS spectrum of 2,4′-BiPy was shown in Fig. 2f. As in the cases of 2,2′-BiPy and 4,4′-BiPy, the out-of-plane ν_{16a}, ν_{16b}, ν_{11}, ν_{17b}, and ν_{10a} bands were found weakly in the Au SERS spectra. Most strong in-plane ring modes have not shown a red shift after adsorption on Au. These results implied a rather weak ring π interaction of 2,4′-BiPy on Au. Also neither a substantial red

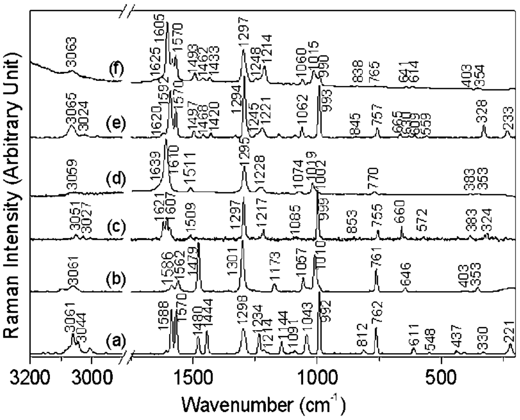

Figure 2. (a) Ordinary Raman spectrum of 2,2′-BiPy in the solid state. (b) SERS spectrum of ~10^{-3} M of 2,2′-BiPy in aqueous gold nanoparticles. (c) Ordinary Raman spectrum of 4,4′-BiPy in the solid state. (d) SERS spectrum of ~10^{-3} M of 4,4′-BiPy in aqueous gold nanoparticles. (e) Ordinary Raman spectrum of 2,4′-BiPy in the solid state. (f) SERS spectrum of ~10^{-3} M of 2,4′-BiPy in aqueous gold nanoparticles. All the spectra were taken using the irradiation at 632.8 nm from a He-Ne laser. Spectral regions between 2900 and 1650 cm^{-1} were omitted due to the lack of any information.

Table 1. Spectral data and vibrational assignment of 2,4′-BiPy

Ordinary raman	Au SERS	Assignment[a]
In-plane		
3065	3063	2 (A_1) (2,4′)
3024		7b (A_1) (2,4′)
1620	1625	8b (A_1) (4′)
1592	1605	8a (A_1) (4′)
1592	1584	8b (A_1) (2)
1570	1570	8a (A_1) (2)
1497	1493	19a (A_1) (4′)
1468	1462	19a (A_1) (2)
1420	1433	19b (A_1) (2)
1294	1297	3 (A_1) (2,4′)
1245	1248	9a (A_1) (2)
1221	1214	9a (A_1) (4′)
1062	1060	12(A_1) (2)
993	1015	12 (A_1) (4′) or 1(A_1) (4′)
993	990	1 (A_1) (2)
665		6b (A_1) (2,4′)
630	641w[b]	6a (A_1) (2′)
609	614w	6a (A_1) (4′)
559		20a (A_1) (2,4′)
		Metal-N
Out-of-plane		
845w	838w	10a (B_1) (4′), 17b (B_1) (2)
757	765w	11 (B_1) (4′)
	403w	16b (B_1) (2)
328	354w	16a (B_1) (4′)

[a] Based on ref. 30 in Wilson notation with symmetries based on C_2 point group. The number in the parenthesis designates the 2 and 4′ pyridyl group, respectively.

[b] w, weak.

shift nor a significant band broadening of the ring breathing ν_1 and ν_{12} modes implied that a direct ring π orbital interaction with gold and silver substrates should be quite low. These results may support a rather vertical orientation of the bipyridine ring in 2,4′-BiPy on gold.

Tables 2 and 3 list the spectral data and appropriate vibrational assignments of 2,2′-BiPy and 4,4′-BiPy, respectively. Since the overall spectral patterns of the three bipyridine compounds are not greatly different from those in their neutral states, their molecular symmetries are assumed to maintain to a certain degree. For the bipyridine compounds, the molecular symmetry can be reduced after adsorption on metal substrates. The D_{2h} symmetry for 4,4′-BiPy could be reduced to $C_{2\nu}$ or C_2 after considering that its two pyridine rings are not assumed to lie on the same plane upon adsorption on surfaces. Considering that the possibility of the interaction between the bipyridine group and gold surfaces is low, the two pyridine rings of 2,4′-BiPy may not be assumed to lie on the same plane either with the C_{2v} or C_2 symmetry.

Since the set of SERS selection rules established so far is highly dependent on the specific enhancement mechanism, it is unfortunate that the structural change cannot be analyzed more precisely from the SERS spectra. The analysis was made herein for a few selected peaks on the basis of the prediction of the electromagnetic (EM) selection rule. From the EM surface selection rule,[22,23] the vibrational mode perpendicular to the surface is more enhanced than the parallel mode. For the three bipyridine compounds, most ring modes were found to belong to the in-plane ones whereas the out-of-plane modes were observed quite weakly. The relative weakness of the out-of-plane bands supported that the adsorbate should have a rather vertical structure.

Table 4 list the intensity ratios with the relevant molecular symmetry elements for 2,2′-BiPy, 2,4′-BiPy, and 4,4′-BiPy, respectively. The ring mode intensities were normalized to the intensity of the ring ν_2 (A_1) mode in each SERS spectrum. As suggested in the recent SERS studies,[24,25] experimental deviations could be alleviated in taking a ratio of the SERS intensities with respect to that of the OR bands obtained at the same excitation wavelengths. The following normalization by the specific mode would be useful to compare the SERS intensities.

2,4′-BiPy appears to adsorb on Au surfaces via the 4-pyridyl nitrogen atom as suggested from the stronger enhancement of the vibrational bands ascribed to the 4-pyridyl ring. 2,4′-BiPy is considered to have a C_2 conformation due to its asymmetry of the nitrogen atom positions assuming an upright structure on Au. The A_1 modes were found to enhance higher than those of the B_1 modes after adsorption on Au for 2,4′-BiPy (Table 4).

Although the SERS spectra feature could be roughly described by the EM mechanism, it is admitted that the CT mechanism may also contribute the SERS intensities of several vibrational bands of the bipyridine compounds on Au. In fact the different enhancement values for the same symmetry as listed in Table 2 could be better explained with a combination of the EM and CT mechanisms. For molecules such as pyrazine[26,27] and phenylacetic acid[28] on silver surfaces, the vibrational band most enhanced by the charge transfer mechanism was calculated to be that of the ν_{8a} mode. It is intriguing that the ν_{8a} mode is found to be most enhanced for 4,4′-BiPy, whereas the intensity is observed to be weakest for 2,2′-BiPy. It was reported that the charge transfer mechanism could also significantly contribute to the enhancement of the SERS intensities.[26–28] The charge transfer would be considered to increase in the order from 2,2′-BiPy, 2,4′-BiPy, and 4,4′-BiPy due to their different positions of the nitrogen atoms as suggested from their disparate ν_{8a} band enhancements upon adsorption on surfaces. As listed in Table 4, the ν_{8a} mode is most enhanced for the present SERS spectrum of 4,4′-BiPy on Au. This quadrant C═C stretching mode along the charge transfer direction

Table 2. Spectral data and vibrational assignment of 2,2′-BiPy

Ordinary raman	Au SERS ($\sim 10^{-3}$ M)	Assignment[a]
In-plane		
3061	3061	2 (A_1)
3044		7b (B_2)
1588	1586	8b (B_2)
1570	1562	8a (A_1)
1480	1479	19a (A_1)
1444		19b (B_2)
1298	1301	3 (B_2)
1234		9a (A_1)
1214		9b (B_2)
1144	1173	14 (B_2)
1091		18b (B_2)
1043	1057	12 (A_1)
992	1010	1 (A_1)
762	761	7a (A_1)
	646	6a (A_1)
611		6b (B_2)
548w[b]		20a (A_1)
330	353	15 (B_2)
	225	Metal-N
Out-of-plane		
812		17b (B_1)
437		16a (A_2)
	403w	16b (B_1)

[a] Based on ref. 30 in Wilson notation with symmetries based on C_{2v} point group. The symmetry in the parenthesis corresponds to C_{2v} point group.

[b] w, weak.

appeared to influence the strong enhancement for 4,4′-BiPy at 1610 cm^{-1}. In contrast, the ν_{8a} band of 2,2′-bipyridine at 1586 cm^{-1} appeared to be extraordinarily less enhanced. This difference could be explained by considering the fact that the vibration of 2,2′-BiPy is assumed to occur quite parallel to the metal surface. Although the electronic states or the changes in the equilibrium geometry for the three bipyridine compounds in the CT process would be dissimilar from those of pyrazine, the SERS enhancements appeared to be better explained by both the EM and CT mechanism .

Fig. 3 shows the UV-vis absorption spectra of gold particles before and after the injection of bipyridine compounds. The UV-vis absorbance spectra measurement condition was analogous to that for SERS experiments. Before the addition of adsorbates, the $\lambda_{\max}$ value was found at 523 nm as in Fig. 3a. After the injection of 4,4′-BiPy, 2,2′-BiPy, and 2,4′-BiPy into an

Table 3. Spectral data and vibrational assignment of 4,4′-BiPy

Ordinary raman	Au SERS ($\sim 10^{-3}$ M)	Assignment[a]
In-plane		
3051	3059	2 (A_1)
3027		7b (B_2)
1621	1639	8b (B_2)
1607	1610	8a (A_1)
1509	1511	19a (A_1)
1297	1295	3 (B_2)
1217	1228	9a (A_1)
1085	1074	18a (A_1)
	1019	12 (A_1)
999	1002	1 (A_1)
660	657w[b]	6a (A_1)
	625w[b]	6b (B_2)
572		20a (A_1)
	235	Metal-N
Out-of-Plane		
853w[b]	854w[b]	10a (A_2)
755	770	11 (B_1)
383	383	16b (B_1)
324	353	16a (A_2)

[a] Based on ref. 30 in Wilson notation with symmetries based on C_{2v} point group.

[b] w, weak.

aqueous gold nanoparticle solution, the UV-vis absorption spectra changed as exhibited in Figs. 3b, c, and d, respectively. The $\lambda_{\max}$ value was red-shifted to ~676, ~707, and ~705 nm, respectively for 4,4′-BiPy, 2,2′-BiPy, and 2,4′-BiPy. Although the UV-vis absorbance spectra exhibited similar prominent shifts for 2,2′-BiPy and 2,4′-BiPy, the spectral behavior for 4,4′-BiPy was found slightly different under our experimental conditions. Fig. 3 exhibits spectral changes of surface plasmon resonance bands resulting from the interparticle aggregation. Aggregation has caused the surface plasmon bands to red-shift from the visible to the near infrared region. In addition, the localized surface plasmon band at 670 ~ 710 nm appears for 2,2′-BiPy, 2,4′-BiPy, and 4,4′-BiPy. This result indicates that the aggregation of the three bipyridine compounds should not be much different for Au nanoparticles. In addition, it is expected that SERS spectra should be effectively enhanced for Au nanoparticles at the wavelengths close to 670 ~ 710 nm due to the overlapping with the plasmon bands

For adsorbed molecules, the CT process is assumed to take place between the ground singlet to the doublet radical anion state.[26,27] Since little is known about the radical anion states of the bipyridine compounds, it is not certain

Table 4. Relative enhancement factors of SERS bands of bipyridine compounds

Symmetry type[a]	Tensor element[b]	Normal mode[c]	Relative Enhancement Factor $(I_{SERS}/I_{OR})^d$ Au SERS ($\sim 10^{-3}$ M)		
			2,2-BiPy	4,4′-BiPy	2,4′-BiPy
A_1 (A_1)	α_{xx}	1 (2)	0.612		0.730
	α_{yy}	1 (4′)		0.623	1.38
	α_{zz}	2 (2,4′)	1.00	1.00	1.00
		12 (2)	2.24		1.21
		12 (4′)			1.38
		6a (2)			0.885
		6a (4′)		0.304	1.34
		7a (2)	2.78		
		8a (2)	0.859		2.24
		8a (4′)		20.2	6.12
		9a (2)			2.31
		9a (4′)		4.74	4.21
		18a (4′)		6.05	
		19a (2)	9.05		1.98
		19a (4′)		7.36	2.75
		20a (2,4′)			
B_1 (A_2)	α_{xy}	10a (4′)		1.81	0.635
		16a (4′)		2.87	0.333
B_1 (B_1)	α_{xz}	11 (4′)		2.89	0.279
		16b (4′)		2.50	
		17b (2)			0.635
A_1 (B_2)	α_{yz}	3 (2,4′)	6.40	5.46	1.32
		14 (2)	2.21		
		15 (2)	9.90		
		8b (2)	0.505		2.20
		8b (4′)		2.65	2.49
		19b			1.87

[a] Symmetry types corresponding to the C_2 point group. The number in the parenthesis corresponds to the C_{2v} point group.

[b] Subscripts, i.e., x, y, and z, correspond to the conventional molecular axes. The x-axis lies perpendicular to the ring, and the z-axis passes through the 4-pyridyl nitrogen atom.

[c] See Table 1 for the vibrational assignment. The number in the parenthesis designates the 2 and 4′ pyridyl group, respectively.

[d] Normalized to 1.00 for the ν_2 band at ca. 3060 cm^{-1} in the SERS and OR spectra.

whether a similar CT process in the case of pyrazine would occur from the metal to vacant orbital of the excited electronic states of adsorbates. The spectral analysis has led to a conclusion that the enhancement mechanism and the electron transfer between the metal substrate and the adsorbate should be different for 2,2′-BiPy, 2,4′-BiPy, and 4,4′-BiPy.

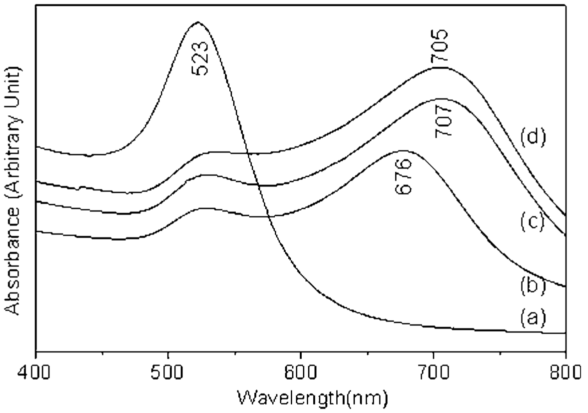

Figure 3. UV-vis absorbance spectral changes of Au nanoparticles (a) before and after the injection of (b) 4,4′-BiPy, (c) 2,2′-BiPy, and (d) 2,4′-BiPy under the similar experimental condition for SERS experiments.

It is quite informative to obtain the SERS excitation profile for manifestations of charge transfer mechanisms as in the case of 2,2′-BiPy on Ag in the wavelength region of 458–600 nm[8]. Under the present experimental conditions, good quality SERS spectra were not obtained for different wavelengths at 488.0 and 514.5 nm using an Ar ion laser, presumably due to the low SERS enhancement factor and localized surface plasmon band shifted to the near infrared region at 670–710 nm for gold particles. Since SERS selection rules do not provide a precise interpretation of band intensities, other spectroscopic techniques have been currently applied to reach a more consistent conclusion. Thermodynamic, electrochemical, and theoretical studies shall also be useful to explain the adsorption characteristics of the bipyridine compounds on Au surfaces.

SUMMARY AND CONCLUSIONS

The adsorption behaviors of 2,2′-bipyridine (2,2′-BiPy), 2,4′-bipyridine (2,4′-BiPy), 4,4′-bipyridine (4,4′-BiPy) on gold nanoparticle surfaces were studied by means of surface-enhanced Raman scattering (SERS). A combination of the electromagnetic (EM) and charge transfer (CT) effects should affect the SERS intensities for the three bipyridines adsorbed on Au nanoparticle surfaces. The enhancement mechanism is assumed to be dissimilar for the three bipyridine compounds due to the disparate positions of their nitrogen atoms as suggested from the different ν_{8a} band enhancements upon adsorption on surfaces. The charge transfer is expected to increase in the order from 2,2′-BiPy, 2,4′-BiPy, and 4,4′-BiPy as suggested from the ν_{8a} band enhancements upon adsorption on surfaces.

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