

# Influence of the Solvent on the Surface-Enhanced Raman Spectra of Ruthenium(II) Bipyridyl Complexes

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In the present work a new dye,  $[\text{Ru}(\text{dcbpyH}_2)_2(\text{bpy-TPA}_2)](\text{PF}_6)_2$ , and the well-known  $(\text{Bu}_4\text{N})_2[\text{Ru}(\text{dcbpyH})_2(\text{NCS})_2]$  complex were investigated. The electronic transitions of both dyes showed solvatochromic shifts due to specific interactions of the ligands with the solvent molecules. The surface-enhanced Raman (SER) spectra of the dyes dissolved in water, ethanol, and acetonitrile were measured in silver and gold colloidal solutions. The results demonstrate that the dyes were adsorbed on the metallic nanoparticles in different ways for different solvents. It was also found that in the gold colloid, the aqueous solutions of both dyes did not produce any SERS signal, whereas in ethanolic solution the SERS effect was very weak. Deprotonation, H-bonding, and donor–acceptor interactions seem to determine these different behaviors. Our results indicate the important role of the charge-transfer mechanism in SERS.

## 1. Introduction

Surface-enhanced Raman scattering (SERS) is a very powerful analytical tool for studying the adsorption of organic molecules on metal surfaces.<sup>1–3</sup> It is widely accepted that SERS is a complex phenomenon that has its origin in two different mechanisms. The first one is the so-called electromagnetic (EM) effect, which is due to resonances of the incident electromagnetic field with the surface plasmons of the metallic nanostructure. This long-range order effect seems to be responsible for the main contribution to the enhancement. The second mechanism is the chemical or charge transfer (CT) effect, which is due to photoinduced dynamic charge transfer between the metal and the molecule. This short-range contribution depends on the nature of the system and the experimental conditions. The chemical interaction seems to play an important role, since not all molecules show SERS spectra, but a selective combination of adsorbed molecule and metal is required.<sup>1</sup> These two mechanisms operate simultaneously giving rise to the total enhancement. SERS data provide highly sensitive information about the orientation of the adsorbate with respect to the metal surface (EM) and about the nature of the interaction of the molecule with the colloidal system (CT).

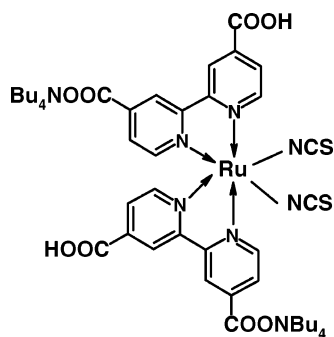
Ruthenium(II) complexes containing polypyridyl ligands have been widely studied as potential photosensitizers in solar cells.<sup>4–7</sup> Of particular interest is their use in dye-sensitized solar cells based on nanocrystalline films of  $\text{TiO}_2$ . The light is absorbed by the dye, then the photoexcited dye molecule transfers an electron to the conduction band of the semiconductor. The injected electrons percolate in the nanocrystalline  $\text{TiO}_2$  to the anode. The oxidized form of the dye is rapidly reduced by redox mediators. Metal-to-ligand charge-transfer transitions dominate the visible absorption spectra of the dyes and the main features of their photophysical and redox behavior. The functional groups of the dye allow for efficient anchoring on the semiconductor surface and promote the electronic com-

munication between the donor orbital of the dye and the conduction band of the semiconductor.

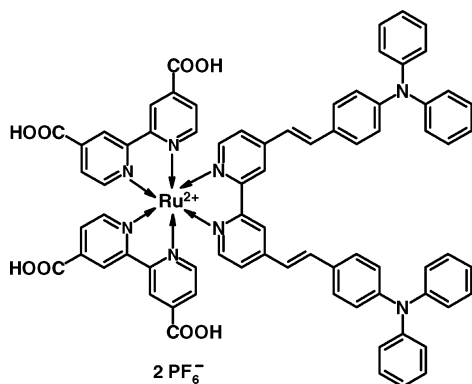
In this work we study the influence of the solvent on the adsorption of two ruthenium dyes on colloidal nanoparticles and their spectroscopic properties. The effects of the solvent on electronic transitions of dye molecules have been extensively studied in the literature; see, e.g., refs 7–13. The wavelength of the absorption maxima of Ru(II) complexes shows solvent-dependent shifts (solvatochromism). Solvatochromic shifts can be large for charge-transfer bands. On the other hand, it was found by Waterland and Kelley using polarized femtosecond transient spectroscopy that the dynamics of the  $[\text{Ru}(\text{dcbpyH}_2)_2(\text{NCS})_2]$  complex is strongly dependent on the solvent and the excitation wavelength.<sup>14</sup> In the work of Streiff and McHale,<sup>13</sup> no solvent dependency was found for any of the vibrational frequencies of the resonance Raman active modes of  $[\text{Ru}(\text{NH}_3)_4\text{-bpy}]^{2+}$ . Webb et al. suggested in ref 15 that a close association of  $[\text{Ru}(\text{bpy})_3]^{2+}$  with water can produce differences in the resonance Raman spectra, which are a fingerprint of the excited state of the dye. The effects of solvent and electrolyte on the Raman spectrum of  $\text{Fe}(\text{phen})_2(\text{CN})_2$  adsorbed on a silver electrode and the adsorption of  $[\text{Ru}(\text{CN})_5(\text{pyS})]^{4-}$  on different substrates and in different solvents were investigated with SER spectroscopy by Corio et al.<sup>16,17</sup> These authors conclude that the chemical nature of solvents and electrolytes plays a decisive role in the SERS of species adsorbed on the electrochemical interfaces, since it can determine the bonding to the surface (electrodes in their case). In our study we investigated dyes with ligands of different nature in order to obtain a better understanding of the influence of the interactions between solvent, complex, and substrate. The role of the different enhancement mechanisms in SERS will be discussed in this context. One of our dyes was the well-known  $(\text{Bu}_4\text{N})_2[\text{Ru}(\text{dcbpyH})_2(\text{NCS})_2]$  photosensitizer with cyano ligands and the other one was a new dye,  $[\text{Ru}(\text{dcbpyH}_2)_2(\text{bpy-TPA}_2)](\text{PF}_6)_2$ , with triphenylamine (TPA) moieties. The TPA unit is often used in organic solid-state dye-sensitized solar cells as a hole conductor.<sup>18,19</sup> Hence, this moiety was attached to the Ru complex as a ligand to improve the

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**Figure 1.** Chemical structure of  $(\text{Bu}_4\text{N})_2[\text{Ru}(\text{dcbpyH})_2(\text{NCS})_2]$  (N719).



**Figure 2.** Chemical structure of  $[\text{Ru}(\text{dcbpyH})_2(\text{bpy-TPA}_2)](\text{PF}_6)_2$  (Ru-TPA<sub>2</sub>).

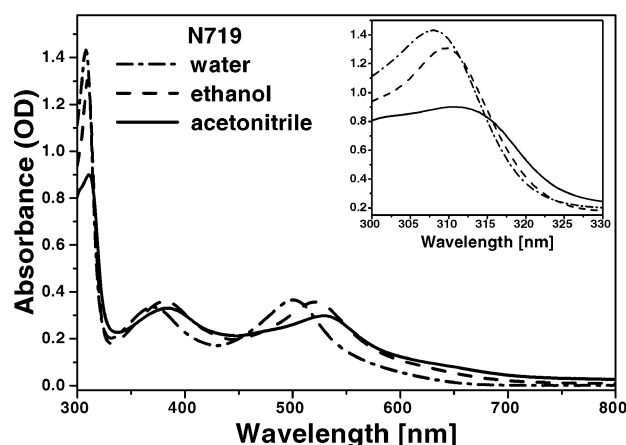
charge transfer to the hole transport layer. A more detailed discussion of the influence of this interface modification in solar cells can be found in refs 18 and 19. As solvents we have used water, ethanol, and acetonitrile, and our SERS substrates were colloidal silver and gold solutions.

## 2. Experimental Section

**2.1. Sample Preparation.** The dye  $(\text{Bu}_4\text{N})_2[\text{Ru}(\text{dcbpyH})_2(\text{NCS})_2]$  ( $\text{Bu}_4\text{N}$  = tetrabutylammonium and dcbpy = dicarboxyphenylpyridine) (N719; see Figure 1) was purchased from Solaronix S.A. (Lausanne, Switzerland) and used as received. The dye  $[\text{Ru}(\text{dcbpyH})_2(\text{bpy-TPA}_2)](\text{PF}_6)_2$  (bpy = bipyridine and TPA = triphenylamine) (Ru-TPA<sub>2</sub>; see Figure 2) was synthesized as described previously.<sup>20,21</sup> All other chemicals involved for sample preparation were purchased from commercial sources (Merck, Sigma-Aldrich) and used without further purification. The gold colloid solution was prepared by reducing  $\text{HAuCl}_4$  with sodium citrate following procedure I described in ref 22. The silver colloid solution was prepared according to ref 23, using 10 mL of  $10^{-2}$  M  $\text{AgNO}_3$  solution, which was added dropwise to 90 mL of a  $3 \times 10^{-3}$  M hydroxylamine hydrochloride ( $\text{NH}_2\text{OH}\cdot\text{HCl}$ ) solution. In both aqueous solutions the measured pH was between 4 and 5.

For measuring the UV-vis spectra, the concentration of the dyes in the different solvents (doubly distilled water, ethanol, or acetonitrile) was less than  $3.5 \times 10^{-5}$  M. For SERS studies, 1:5 mixtures of dye solution/aqueous colloidal solution were prepared. The concentration of the complexes in the colloidal solutions was below  $6 \times 10^{-6}$  M. Both absorption and SERS experiments were carried out in quartz cuvettes with 1 cm thickness.

In addition, UV-vis, normal Raman, and SERS spectra of tetra-*n*-butylammonium iodide, triphenylamine (TPA), and bpy-TPA<sub>2</sub> were measured to provide further spectral information.



**Figure 3.** Absorption spectra of N719 in different solvents. The inset shows the intraligand charge-transfer bands on an enlarged wavelength scale.

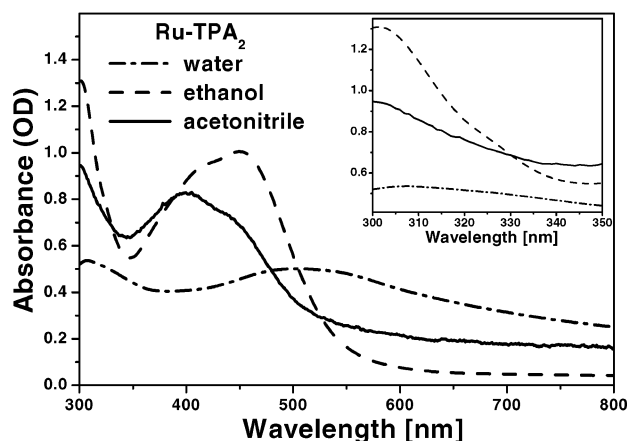
**2.2. Spectroscopic Measurements.** UV-vis absorption spectroscopy was performed with a Perkin-Elmer UV/VIS/NIR spectrophotometer. Scan rates were 240 nm/min. The spectral resolution was 2 nm over the spectral region of interest.

For measuring the Raman spectra we used a custom-built confocal setup similar to that described previously.<sup>24</sup> It is centered around an inverted microscope Swift M100. PlanApo objectives  $4\times/0.18$ ,  $10\times/0.45$ ,  $20\times/0.75$ , and a Leica PL Fluotar  $100\times/0.75$  were used for focusing the laser and collecting the scattered light. The setup was equipped with a HeNe laser ( $\lambda = 632.8$  nm) providing an effective power of 3.2 mW on the sample. In some of the measurements this power was reduced to avoid light-induced modifications of the dyes. Spectral dispersion was performed in a single monochromator (Acton Research SpectraPro-500i) with a grating of 300 grooves per mm, yielding a resolution of  $2.6 \text{ cm}^{-1}$ . The entrance slit of the monochromator was replaced with a  $50 \mu\text{m}$  pinhole for confocal depth selection. The Rayleigh line was suppressed by a factor of  $10^6$  with a holographic notch filter (Kaiser Optical Systems). Raman spectra were recorded with a liquid nitrogen cooled CCD detector with  $1340 \times 100$  pixels (Princeton Instruments). All spectra presented in this paper are the sum of six spectral accumulations, each with 10 s integration time. All experiments were performed at room temperature.

## 3. Results and Discussion

**3.1. Absorption Spectra.** UV-vis absorption spectra of the investigated dyes in different solvents (water, ethanol, and acetonitrile) are shown in Figures 3 and 4. The weaker absorption of the complex Ru-TPA<sub>2</sub> in water is a consequence of its poor solubility in this solvent. In the visible region, the spectra of Ru(II) complexes containing polypyridyl ligands are dominated by bands arising from metal-to-ligand charge-transfer (MLCT) transitions, in which an electron is promoted from a ruthenium  $d\pi$  orbital to the  $\pi$  system of the polypyridyl ligand. The bands in the UV are due to intraligand transitions ( $\pi \rightarrow \pi^*$ ). The band energies are listed in Table 1.

The energies and, in the case of Ru-TPA<sub>2</sub>, also the shapes of the MLCT bands are strongly solvent dependent, whereas the shifts of the intraligand bands are less pronounced. The solvent dependence of the wavelength of electronic transitions (solvatochromism) has been extensively studied in the literature.<sup>7-13</sup> The solvatochromic shifts can be large for charge-transfer bands, as was discussed in detail in a review article by Chen and Meyer.<sup>12</sup> If the solvent can be approximated by a dielectric



**Figure 4.** Absorption spectra of Ru-TPA<sub>2</sub> in different solvents. The inset shows the intraligand charge-transfer bands on an enlarged wavelength scale.

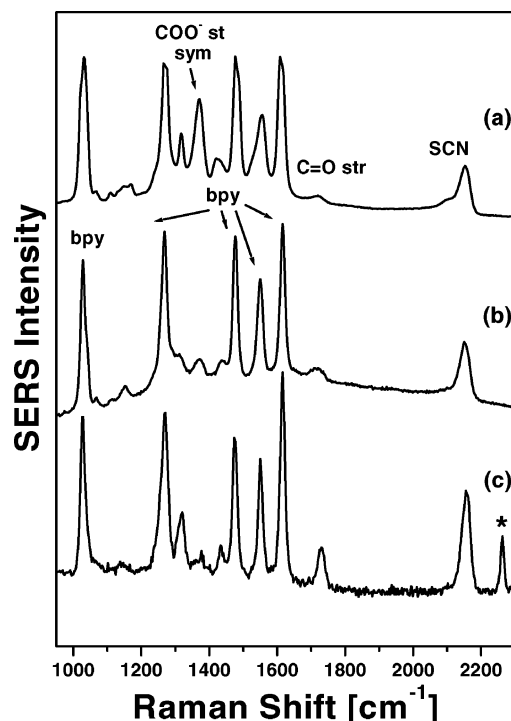
**TABLE 1: Absorption of N719 and Ru-TPA<sub>2</sub> in Different Organic Solvents at Room Temperature**

complex/solvent	absorption maxima [nm]		
	intraligand CT	MLCT	
N719/H <sub>2</sub> O	308	370	500
N719/C <sub>2</sub> H <sub>5</sub> OH	309	381	521
N719/CH <sub>3</sub> CN	311	383	529
Ru-TPA <sub>2</sub> /H <sub>2</sub> O <sup>a</sup>	307	507	
Ru-TPA <sub>2</sub> /C <sub>2</sub> H <sub>5</sub> OH <sup>a</sup>	299	396	461
Ru-TPA <sub>2</sub> /CH <sub>3</sub> CN <sup>a</sup>	294	394	451

<sup>a</sup> Calculated with a Lorentzian fit.

continuum, one can calculate its contributions to these shifts from the known geometry of the solute and the dielectric properties of the solvent. But the dielectric continuum theory breaks down for charge transfer in amine or cyano complexes, because there are specific interactions between these ligands and the individual solvent molecules. These interactions exist in addition to the continuum effects and tend to dominate; hence, correlations with dielectric functions normally fail. Specific interactions arise from H-bonding or donor–acceptor interactions. In both cases, orbital mixing occurs between individual ligands and solvent molecules. Given the nature of the specific interactions, the donor number (DN) and acceptor number (AN) introduced by Gutmann are useful parameters for correlating MLCT solvent shifts. The Gutmann donor and acceptor number are dimensionless quantities which provide a relative measure of the Lewis acidity (electron pair acceptor ability) of the solvent.<sup>25</sup>

The N719 transitions perform a blue shift with increasing Gutmann acceptor number. This effect can be due to the H-bonding of solvent molecules to the electron pair of the thiocyanate sulfur, as previously noted for other cyano and thiocyanate complexes.<sup>7,12,16</sup> This dependence increases with the number of CN ligands.<sup>12</sup> For water, AN = 54.8; for ethanol, AN = 37.1; and for acetonitrile, AN = 19.3.<sup>25</sup> Deprotonation of this dye also produces shifts of the MLCT bands toward the UV region, as was observed in ref 26. Amine complex transitions, on the other hand, usually exhibit a red shift of the absorption band energies with increasing Gutmann donor number of the solvent. This correlation has been ascribed to the H-bonding of the solvent with the amine groups.<sup>12,13</sup> As in the case of cyano complexes, the correlation increases with the number of amine ligands.<sup>12</sup> In the Ru-TPA<sub>2</sub> solutions, water seems to act as if it had a higher donor number, causing a larger shift than ethanol. For water, DN = 18.0; for ethanol, DN =



**Figure 5.** SERS of N719 in (a) water(I), (b) water(II), and (c) acetonitrile with the silver colloid. The behavior in ethanol is similar as in water. The asterisk indicates the line of acetonitrile

20; and for acetonitrile, AN = 14.1.<sup>25</sup> The deprotonation state of the dyes will be discussed below.

**3.2. Raman Spectroscopy.** It is generally accepted that excitation wavelengths in the red are preferred for SERS measurements on gold and copper, whereas green light is mostly used on silver. Nevertheless, all the Raman spectra of the present work (normal Raman and SERS experiments) have been recorded with the 632.8 nm line of a HeNe laser.

The absorption spectra of the dyes (Figures 3 and 4) show that at this wavelength no significant contribution of resonance effects is expected (except for few cases which will be discussed later). Moreover, the low absorption in this region reduces the probability of photodecomposition and other light-induced phenomena. The choice of the HeNe laser allows us to compare directly the results measured on silver and gold. Results of further investigations with excitation of 532 nm and, therefore, with the contribution of preresonance and resonance effects will be presented in a future publication. The normal Raman spectrum of Ru-TPA<sub>2</sub> powder was directly measured with the HeNe laser. The vibrational bands were analyzed after subtracting the pronounced fluorescence background using fitting procedures. The normal Raman spectrum of N719 powder could not be measured due to very strong fluorescence.

**3.3. SERS in Silver Solution.** When the dye solutions were added to the aqueous colloidal solutions to produce the final SERS samples, sometimes aggregation occurred<sup>27</sup> leading to precipitation of the metal nanoparticles with the adsorbed dye. The spectra could then be measured either in the solution or by focusing on the precipitate. Usually the signals were identical, but in the spectra obtained from the precipitate, the lines of the solvents were less pronounced and better spectra could be recorded. In the case of N719, however, slightly different signals were measured, when the solvent was water or ethanol (see Figure 5). For water, the signal recorded in the precipitate is marked as water(I) and that of the solution as water(II). The behavior in ethanol is similar as in water. We present the spectra



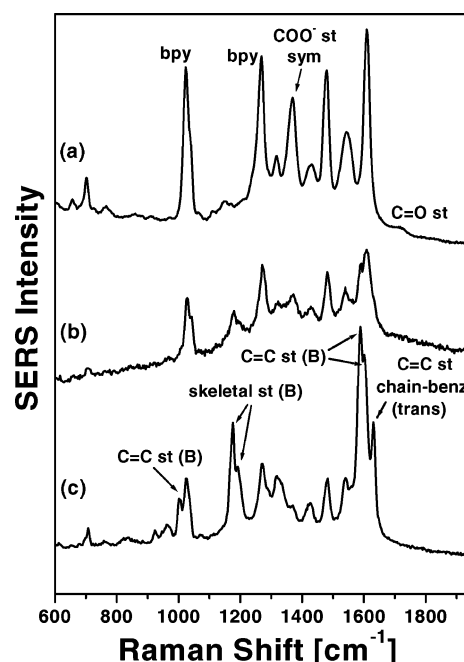
in water, since the H<sub>2</sub>O lines have almost no overlap with the lines of the dye in the spectral region of interest.

It is found that the bipyridine lines predominate in the SERS spectra of N719, as was already reported by other authors for RS,<sup>28</sup> RRS,<sup>29</sup> SERS,<sup>6,30,31</sup> and SERRS<sup>32</sup> experiments on the same dye and similar complexes. Minor differences in the intensities of these bands are present between the spectra of the complex in different solvents. The symmetric stretching mode  $\nu(\text{COO}^-)$  appears in the aqueous solution, whereas it is completely missing in acetonitrile. The  $\nu(\text{C}=\text{O})$  mode shows the opposite behavior; its intensity decreases from acetonitrile to water. The thiocyanate band at  $\sim 2150\text{ cm}^{-1}$  varies in the same way, and in the water-(I) spectrum it shows a shoulder at lower frequencies.

In the article of Finnie et al.,<sup>28</sup> the regular Raman spectra of  $[\text{Ru}(\text{dcbpyH}_2)_2(\text{NCS})_2]$ ,  $(\text{Bu}_4\text{N})_2[\text{Ru}(\text{dcbpyH}_2)_2(\text{NCS})_2]$ , and  $(\text{Bu}_4\text{N})_4[\text{Ru}(\text{dcbpy})_2(\text{NCS})_2]$  powders were recorded with an excitation wavelength of 1064 nm. If we compare our results with those of Finnie et al., we can conclude that the dye behaves as fully protonated in acetonitrile and partially or completely deprotonated in water and ethanol.

The  $\text{pK}_a$  of  $[\text{Ru}(\text{dcbpyH}_2)_2(\text{NCS})_2]$  (fully protonated complex) determined by UV/VIS and emission measurements of a 1:5 ethanol/H<sub>2</sub>O mixture solution of the complex was reported in ref 7. Taking into account that the dissociation of the carboxy groups occurs stepwise, the authors concluded that the first deprotonation step (one carboxy group of each dcbpy unit) takes place at  $\text{pK}_a = 1.5$  and the second step (all carboxylic groups are dissociated) at  $\text{pK}_a = 3$ . According to these results, the majority of the  $(\text{Bu}_4\text{N})_2[\text{Ru}(\text{dcbpyH}_2)_2(\text{NCS})_2]$  molecules at pH values of 4–5 of our aqueous and ethanolic solutions should be completely dissociated. For the acetonitrile solution, however, some correction factors have to be included. The  $\text{pK}_a$  values increase with increasing the concentration of the organic solvents, as was discussed in ref 33. The presence of acetonitrile as a cosolvent produces a stronger effect on the  $\text{pK}_a$  values than other organic cosolvents studied (e.g. ethanol). This behavior is mainly attributed to two effects: solute–solvent interaction and proton–solvent interaction. Acetonitrile is considered to be both a poorer acceptor and a poorer donor of hydrogen bonds as compared to water. Thus, acetonitrile is not able to stabilize the carboxylate groups, since it cannot establish H-bonds with them (*solute–solvent interaction*). On the other hand, acetonitrile is a very weakly basic solvent and does not favor the dissociation of the carboxylic acid (*proton–solvent interaction*). In the cited work,<sup>33</sup> the dissociation constants for some dicarboxylic acids in various hydroorganic media were measured. The correction factors of the  $\text{pK}_a$  of a 1:5 acetonitrile/H<sub>2</sub>O mixture were between 0.7 and 1.5 as compared to the pure water solution, and between 0.3 and 0.9 as compared to 1:5 ethanol/H<sub>2</sub>O. Thus, we can conclude that in our acetonitrile solutions the majority of the molecules are not completely dissociated.

After this first overview of the state of the dye in the different solvents, we continue with a more detailed analysis of the observed spectra. In acetonitrile the complex is partially protonated, but the  $\text{COO}^-$  vibrations (with delocalized charges) cannot be seen. On the other hand, the  $\text{C}=\text{O}$  vibration of the undissociated carboxylic acid (with localized charges) is strongly enhanced. A very strong thiocyanate band is found at  $2156\text{ cm}^{-1}$ , significantly shifted in comparison with the position at  $\sim 2100\text{ cm}^{-1}$  as measured in previous spectroscopic studies of this dye.<sup>4,7,28</sup> This indicates that the molecule is adsorbed via its NCS groups, which have free electron pairs. Binding through its carboxylate moieties does not seem to occur. The solvent



**Figure 6.** SERS of Ru-TPA2 in (a) ethanol, (b) water, and (c) acetonitrile with the silver colloid.

molecules surround the carboxy groups and keep the  $\text{Bu}_4\text{N}$  unit *bound or attached* to the  $\text{COO}^-$ , thus avoiding direct contact with the colloidal surface. The lack of signals of the deprotonated forms could be explained with the help of the surface selection rules of the EM mechanism. The vibrations perpendicular to the surface are more strongly enhanced than the parallel modes. Taking this into account, we can expect that the dissociated carboxy groups are tilted with respect to the rest of the molecule, which must be perpendicular to the metallic surface.

In water and in ethanol the dye also binds through its  $\text{COO}^-$  moieties, as can be deduced from the observation of the symmetric stretching mode of the  $\text{COO}^-$  group at  $1370\text{ cm}^{-1}$ . Two different spectra can be distinguished, the spectrum in the water solution (II), where the complex appears to be half deprotonated, and that measured in the water-dye precipitate (I), where it is found to be almost completely dissociated. In the first spectrum (water(II)), the  $\text{COO}^-$  line begins to appear, whereas the thiocyanate and the  $\text{C}=\text{O}$  line decrease in intensity. In the second type (water(I)), the  $\text{C}=\text{O}$  band is almost absent, and a shoulder at lower frequencies ( $\sim 2100\text{ m}^{-1}$ ) appears on the  $\nu(\text{SCN})$  line showing the presence of nonequivalent thiocyanate groups. We ascribe these lines to the SCN groups which are either free or bonded to metallic particles, respectively.

The SERS spectra of the Ru-TPA<sub>2</sub> complex in different solvents with the silver colloid are shown in Figure 6. This complex also appears to be adsorbed on the metallic nanoparticles in different ways for different solvents, as was discussed before for the N719. The different binding behavior has a bigger influence on the Ru-TPA<sub>2</sub> spectra due to its structure (see Figure 2). The  $\text{pK}_a$  of this dye is unknown, but from the similar structure we assume that it should be close to the values measured for the N719 complex. We would like to stress that for this complex the signals in ethanol and in water are different.

When the dye is dissolved in acetonitrile, the SERS signal corresponds mainly to the bpy-TPA<sub>2</sub> part and the lack of the strong bpy lines can be noticed. The complex behaves as if it is fully protonated, and seems to attach to the silver particle only via its donor ligands, the TPA (triphenylamine), whose

**TABLE 2: Raman Shift [cm<sup>-1</sup>] and Assignment of the Band Observed in SERS Spectra of N719 in Different Solvents, in Silver and Gold Solutions at 632.8 nm Excitation<sup>a</sup>**

powder (ref 28) (normal Raman)	SERS/H <sub>2</sub> O <sup>b</sup> (Ag soln)	SERS/CH <sub>3</sub> CN (Ag soln)	SERS/CH <sub>3</sub> CN (Ag soln)	vibrational assignment
2100	2153 (m)	2156 (s)	2142 (vs)	$\nu(\text{CN})$ (SCN)
1723	2092 (w)			$\nu(\text{CN})$ (SCN)
1609	1710 (vw)	1729 (m)	1728 (s)	$\nu(\text{C}=\text{O})$
	1615 (vs)	1616 (vs)	1615 (vs)	$\nu(\text{C}=\text{C})$ (bpy)
	1555 (m)			$\nu(\text{COO}^-)$ asym ?
1545	1540 (sh)	1550 (m)	1550 (m)	$\nu(\text{C}=\text{C})$ (bpy)
1470	1478 (vs)	1476 (vs)	1477 (vs)	$\nu(\text{C}=\text{N})$ (bpy)
1413	1420 (w)	1430 (w)	1427 (w)	$\nu(\text{C}=\text{N})$ (bpy)
1364 (IR)	1370 (m-s)			$\nu(\text{COO}^-)$ sym
1304	1318 (w)	1319 (w)	1320 (w)	$\nu(\text{C}=\text{N})$ (bpy)
1266	1270 (vs)	1268 (vs)	1267 (vs)	$\nu(\text{C}=\text{C})$ intern-ring (bpy)
	1030 (vs)	1028 (vs)	1028 (vs)	ring breathing (bpy)

<sup>a</sup>  $\nu$  = stretching, s = strong, m = medium, w = weak, v = very, sh = shoulder. <sup>b</sup> Water(I).

**TABLE 3: Raman Shift [cm<sup>-1</sup>] and Assignment of the Band Observed in the Powder and in SERS Spectra of Ru-TPA<sub>2</sub> in Different Solvents, in Silver and Gold Solutions at 632.8 nm Excitation<sup>a</sup>**

powder (normal Raman)	SERS/C <sub>2</sub> H <sub>5</sub> OH (Ag soln)	SERS/CH <sub>3</sub> CN (Ag soln)	SERS/CH <sub>3</sub> CN (Au soln)	vibrational assignment
	1704 (vw)			$\nu(\text{C}=\text{O})$
1633 (m)		1630 (s)	1629 (s)	$\nu(\text{C}=\text{C})$ (C-H chain, trans)
	1609 (vs)			$\nu(\text{C}=\text{C})$ (bpy)
1606 (vs)		1603 (vs)	1603 (vs)	$\nu(\text{C}=\text{C})$ (B) + $\nu(\text{C}=\text{C})$ (bpy)
1588 (vs)		1586 (vs)	1586 (vs)	$\nu(\text{C}=\text{C})$ (B) + $\nu(\text{C}=\text{C})$ (bpy)
	1556 (sh)			$\nu(\text{COO}^-)$ asym ?
1537 (m)	1540 (m)	1539 (m)	1540 (m)	$\nu(\text{C}=\text{C})$ (bpy)
1490 (m)	1478 (vs)	1480 (m)	1488 (m)	$\nu(\text{C}=\text{N})$ (bpy)
1425 (w)	1422 (w-m)	1420 (w-m)	1425 (w-m)	$\nu(\text{C}=\text{N})$ (bpy)
	1366 (s)			$\nu(\text{COO}^-)$ sym
1330 (w)		1323 (m)	1326 (m)	$\delta(\text{C}-\text{H})$ (C-H chain)
	1316 (w-m)			$\nu(\text{C}=\text{N})$ (bpy)
1273 (m)		1281 (m)	1280 (m)	$\nu(\text{C}-\text{N})$ (B)
	1266 (vs)			$\nu(\text{C}=\text{C})$ intern-ring (bpy)
1190 (sh)		1194 (m)	1193 (m)	$\nu_{\text{skeletal}}$ (B)
1175 (s)		1173 (s)	1173 (s)	$\nu_{\text{skeletal}}$ (B)
1024 (m-s)	1025 (vs)	1026 (m)	1026 (m)	$\delta(\text{C}-\text{H})$ (bpy)
		1000(m)	1002 (w)	$\nu(\text{C}=\text{C})$ sym (B)

<sup>a</sup>  $\nu$  = stretching,  $\delta$  = deformation, s = strong, m = medium, w = weak, v = very, sh = shoulder.

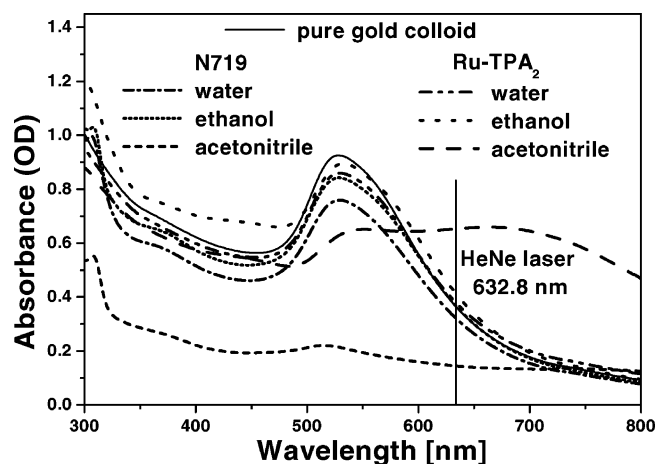
nitrogen atom shows a high affinity to silver. In water it behaves as half or fully deprotonated; the molecule can also bind through its COO<sup>-</sup> groups, and a mixture of the signals as observed in acetonitrile and in ethanol is measured. In ethanol, it is almost completely deprotonated. Both bonding mechanisms are possible, but the affinity of the carboxylate groups to silver appears to be higher, and only the signal corresponding to the [Ru-(dcbpy)<sub>2</sub>] part can be observed. Hence, this spectrum is very similar to that of N719. A very weak  $\nu(\text{C}=\text{O})$  shoulder appears in it, indicating that there are still a few protonated carboxy groups present. It is noticeable that in acetonitrile we could not observe the dicarboxybipyridine part, and in ethanol no signal of the TPA arms was seen. Taking into account the EM surface selection rules would not be sufficient to explain the recorded spectra; the chemical or charge-transfer mechanism must be considered to understand these strong differences.

The fact that the dyes are adsorbed on the colloidal systems in different ways depending on the solvent can be attributed to two different effects. The first one is the solute-solvent interactions which produce variations in the pK<sub>a</sub> values and result in differences of the protonation state of the complexes as discussed previously. In ref 34 the SER spectra of thiophene-2-carboxylic acid were studied at different pH, suggesting that the adsorption geometry is pH dependent, since the molecules were chemisorbed on the metal through different groups. The second effect is H-bonding and donor-acceptor interactions which seem to play an important role in a similar way as for

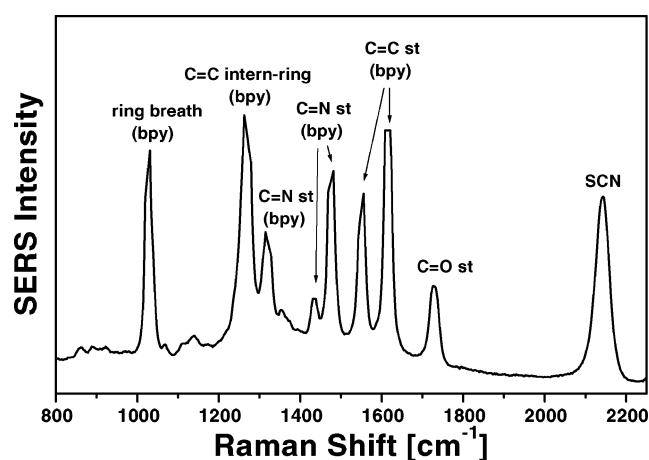
the electronic transitions of the dyes. In acetonitrile, which is an acceptor for hydrogen bonds, the dyes bind through their electron-donor ligands. In water, which is both a hydrogen bond acceptor and a hydrogen bond donor solvent, the complexes also bind through their electron-acceptor ligands. Finally in ethanol, a hydrogen bond donor, the Ru-TPA<sub>2</sub> complex only binds through its electron-acceptor ligands, whereas the N719 still binds via both ligands.

We wish to mention that the  $\nu(\text{OH})$  line of the carboxylic acid groups was not observed in any of the recorded spectra. In some cases it might overlap with the OH bands of the water, but in the majority of the measurements these bands were not seen either. Moreover, also the signals of tetrabutylammonium (Bu<sub>4</sub>N) were not observed, except for the symmetric and asymmetric stretching modes  $\nu(\text{C}=\text{H})$  at 2870 and 2970 cm<sup>-1</sup>, respectively, which appear in some of the measured spectra. A further discussion of the bands and their vibrational assignment is contained in Table 2 for N719 and in Table 3 for Ru-TPA<sub>2</sub>. Several publications were used for the band assignment.<sup>6,7,28-30,32,35,36</sup>

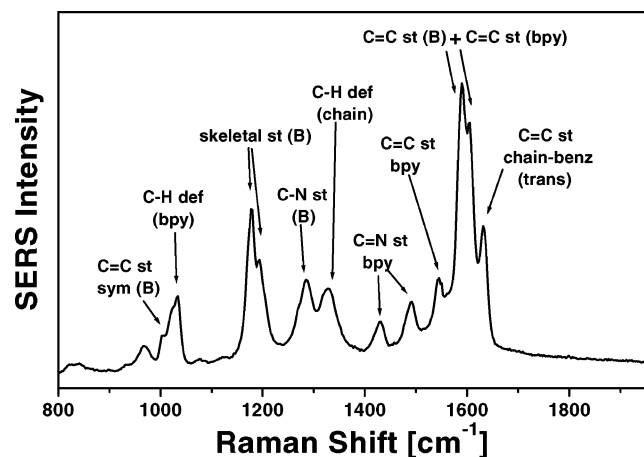
**3.4. SERS in Gold Solution.** In the aqueous gold solutions of both dyes no SERS signal was observed at all, and in the ethanolic solution the SERS effect was very weak. In acetonitrile, on the other hand, the enhancement was very strong and the spectra of both dyes could readily be measured. This can be related with the markedly different UV/VIS spectra of the two acetonitrile gold solutions in Figure 7. The vibrational



**Figure 7.** Absorption spectra of the gold colloid solution with N719 and Ru-TPA<sub>2</sub> complexes in different solvents.

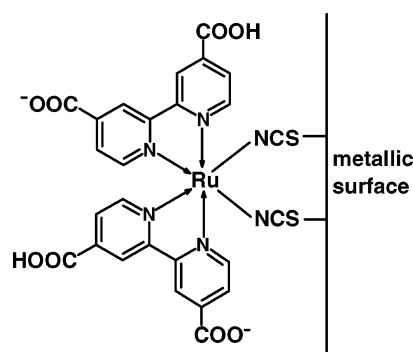


**Figure 8.** SERS spectrum of N719 in acetonitrile with the gold colloid.

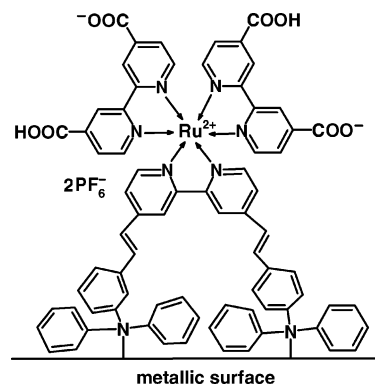


**Figure 9.** SERS spectrum of Ru-TPA<sub>2</sub> in acetonitrile with the gold colloid.

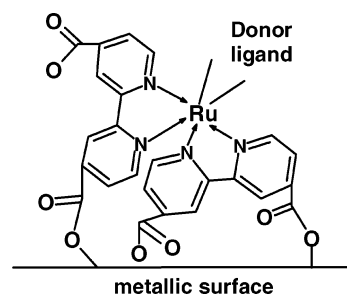
spectra did not show pronounced qualitative differences from the signals recorded in the silver solutions; only quantitative changes occurred. In the spectrum of N719, the  $\nu(\text{CN})$  band of the thiocyanate group at  $\sim 2150 \text{ cm}^{-1}$  turned out to be much stronger and slightly blue-shifted as compared to the silver solution (see Figure 8). This might be related to a stronger binding of the SCN group to Au than to Ag, as was observed in other studies of Au/SCN and Ag/SCN systems.<sup>17,37</sup> The Raman spectrum of Ru-TPA<sub>2</sub> is also affected by resonance enhancement (SERRS) effects (see Figure 9). The SERRS



**Figure 10.** Sketch of N719 adsorbed on the metallic nanoparticle when dissolved in acetonitrile.



**Figure 11.** Sketch of Ru-TPA<sub>2</sub> adsorbed on the metallic nanoparticle when dissolved in acetonitrile.



**Figure 12.** Sketch of the dyes adsorbed on the metallic nanoparticle when dissolved in water or ethanol.

spectrum measured in gold is very similar to the SERS spectrum obtained in silver indicating that the CT mechanism is present in both effects, playing an important role in the enhancement of the Raman signals.

It is well-known that the SERS effect is stronger with silver than with other metals. Nevertheless, the complete absence of SERS signals in aqueous solutions and the weak effect in ethanol is very surprising. Apparently, the interaction with gold is not strong enough to break the hydrogen bonds between the carboxylic groups and the solvent molecules. In ref 8 it was mentioned that the amine ligands also form H bonds with the solvent molecules and that these bonds produce shifts of the electronic transitions (solvatochromism), as we discussed in the first part of this section. In addition, H-bonding of the solvent molecules to the electron pair of the thiocyanate sulfur can occur, which prevents the NCS groups from attaching to the metallic nanoparticles. Strong hydrogen bonding of hydroxylic solvents with CN moieties was also reported by Corio et al. in ref 16. This hydrogen bonding is less efficient in ethanol, however. Ethanol is a weaker Lewis acid than water, which explains that some contact of the dye with the metallic surface is possible.

Qualitative sketches of the adsorption of the molecules on the metallic surface for different solvents are presented in Figures 10–12.

#### 4. Conclusions

UV–vis absorption experiments showed solvatochromic shifts of the electronic transitions of the two dyes due to H-bonding and donor–acceptor interactions between the ligands and the solvent molecules. The N719 transitions exhibit a blue shift with increasing Gutmann acceptor number, as was already observed for other cyano and thiocyno complexes. In contrast, the Ru-TPA<sub>2</sub> transitions show a red shift with increasing Gutmann donor number of the solvent, except for water, which causes a larger shift than ethanol. An extra contribution owing to the different deprotonated states of the dyes has also to be taken into account.

The analysis of the recorded spectra reveals that the dyes are adsorbed on the colloidal systems in different ways depending on the solvent. When dissolved in acetonitrile (hydrogen bond acceptor solvent), the dyes do not deprotonate completely and bind via their electron-donor ligands, whereas in water (both hydrogen bond donor and hydrogen bond acceptor solvent) they also bond via their electron-acceptor ligands. In ethanol (hydrogen bond donor solvent), N719 has the same behavior as in water, whereas Ru-TPA<sub>2</sub> only binds through its electron-acceptor ligands.

We have also found that in aqueous gold solutions of the dyes no SERS signal was produced and in ethanolic gold solutions the SERS effect was very weak. This can be ascribed to the smaller affinity of the complexes to gold as compared to silver, which apparently has the consequence that the interaction between dye and gold nanoparticle is not strong enough to break the hydrogen bonds between the dye and the solvent molecules. The similarities of the SERS and the SERRS signals of the Ru-TPA<sub>2</sub> indicate the important role of the chemical mechanism. Charge transfer, H-bonding, and donor–acceptor interactions are crucial to interpret the observed spectra.

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