Photoactivated nano-systems: self-assembled nano-scaled systems through cyclodextrin complexation, functionalized nanoparticles and hydrogen evolution
Contreras Carballada, P.

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Nano-sized Cyclodextrin Systems for Self-Assembly Studied with Raman Spectroscopy*

Abstract

This chapter presents Raman Spectroscopy performed on metal nanoparticles interacting with compounds designed to assemble on the surfaces of the particles. The metal nanoparticles are stabilized with thiolated β-cyclodextrins. This stabilizer makes the metal particles water soluble in the form of a metal colloid (Pt or Au) and presents a binding site for appropriate guest compounds. We have studied the interactions with a viologen compound functionalized with adamantane, ada-MV, and a ruthenium tris-bipyridyl complex functionalized with a biphenyl-tail, Ru(bpy). For the combination of functionalized gold nanoparticles and the ada-MV compound we have determined strongly shifted Raman bands indicating interaction of the components with the surface of the metal particles.

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5.1 Introduction

The supramolecular organization of chromophoric units self assembled on metallic nanostructures aims to introduce specific functions like the conversion of incident light into electricity or fuel such as hydrogen-gas.\textsuperscript{1, 2, 3} Many of these systems are inspired by the natural photosynthetic systems\textsuperscript{4} in which, in order to harvest all the light energy, large numbers of chromophores self organize in arrays of determined geometry. The combination of active nanostructures and supramolecular organization of chromophores drives modern catalytic concepts\textsuperscript{5} based on bio-mimetic function.\textsuperscript{6, 7}

This chapter describes SERS (Surface Enhance Raman Spectroscopy) investigations of photo and electro-active compounds and their supramolecular organization on noble metal nanoparticles. In fact Raman spectroscopy could allow us to characterize the components and assemblies to reveal possible electronic interaction between the nanoparticle and the chromophoric unit. For this purpose thiol functionalized \(\beta\)-cyclodextrin (\(\text{TCD}\), all primary hydroxyl groups are substituted for thiol groups) and adamantane functionalized methyl-viologen (\(\text{ada-MV}\)) were used as well as a ruthenium tris-bipyridyl derivative with a biphenyl guest tail (\(\text{Rubph}\)). As metals gold was chosen for its excellent properties as substrate for SERS and platinum for its interesting properties when applied in catalysis.

The \(\text{TCD}\) molecules have been reported by Reinhoudt et al.\textsuperscript{8} and have proven to be very interesting hosts for surface functionalization.\textsuperscript{9} Kaifer et al. first described the stabilization of metal colloids with these \(\text{TCD}\) molecules and the possibility of using them as building blocks in self assembled nano-structures.\textsuperscript{10} The \(\text{ada-MV}\) compound was reported previously\textsuperscript{11} by Park \textit{et al.} Adamantyl compounds are know to form host-guest complexes with \(\beta\)-cyclodextrins\textsuperscript{12} with high association constants in the order of \(10^3\)-\(10^4\) M\(^{-1}\) and also it is already known that methylviologen derivatives can be used for electron transfer processes as e.g. for the production of \(\text{H}_2\). Methylviologen (\(\text{MV}\)) was used as a control compound since it does not bind to the cyclodextrin with the same strength as \(\text{ada-MV}\). For the ruthenium tris-bipyridyl complex with a biphenyl guest unit (\(\text{Rubph}\)) the biphenyl residue can also bind the cyclodextrin cavity due to hydrophobic interaction.
and the ruthenium complex is an outstanding complex for its photophysical properties. The biphenyl tail has been used before in the study of photoinduced processes between hosts and guests. The structures of the compounds used here are shown in figure 5.1.

![Figure 5.1. Compounds used in this study. TCD, adamantane functionalized viologen (ada-MV) and a ruthenium tris-bipyridyl complex functionalized with a biphenyl guest tail (Rubph). The drawings are not on the same scale.](image)

SERS is a technique that has been applied to several systems on metal surfaces and colloids. It allows the study of Raman signatures of molecules when they are in close proximity to a surface. When a molecule is immobilized on a SERS metal such as gold, silver or copper, the interaction of the surface plasmon band of the metal surface with the incoming/outgoing electromagnetic radiation has a cooperative effect enhancing the interaction of the exciting radiation with the substrate, amplifying the resulting Raman spectrum, sometimes by several orders of magnitude. The first observation of this effect was made during a study of the adsorption of pyridine on a silver electrode. The authors describe how the Raman signature of pyridine has a great intensity increase when the compound is adsorbed on the electrode surface. The enhancement intensity of the Raman signal depends among others on the shape of the substrate or the proximity of a molecule to one of the substrate’s “hot spots”. Calculations for the location of such “hot spots” on metal particles of different shapes and sizes show a higher intensity of electromagnetic...
field closer to irregularities/spikes of the particle surface or in between particles that are nearly touching.\textsuperscript{17} A theoretical description of the enhancement of Raman scattering by molecules absorbed at the surface of isolated metal spheres and spheroids has been developed by Kerker and coworkers\textsuperscript{18,19}. In this description the SERS effect owes its high intensity to an enhancement of the electromagnetic fields at the metal surface, due to resonant response of the particle to the incident light and further resonant response to the outgoing Raman scattered light. In the simplest case of spherical particles within the dipole limit (for particles much smaller than the wavelength, the particle behaves as if it were a polarizable dipole) the Raman enhancement factor $G$ is given by equation (1):

$$G = \left[ 1 + \frac{2(\varepsilon_r - 1)}{\varepsilon_r + 2} \right]^{\frac{1}{2}} \left[ 1 + \frac{2(\varepsilon_r - 1)}{\varepsilon_r + 2} \right]^{\frac{1}{2}}$$

(1)

Where $\varepsilon_i$ and $\varepsilon_r$ are the values of the metal complex dielectric function relative to the surrounding medium at the incident and Raman scattered frequencies. In predicting the value of $G$ we must bear in mind however that the values of these dielectric constants are commonly obtained from measurements on bulk samples and may not be valid for small particles because of quantum size effects.\textsuperscript{20}

The same formula can be expressed as:

$$G = \left[ 1 + 2g \right] \left[ 1 + 2g_0 \right]$$

(2)

where:

$$g = \frac{m^2 - 1}{m^2 + 2} \quad g_0 = \frac{m_0^2 - 1}{m_0^2 + 2}$$

(3) and (4)

These expressions are valid only when the particles are much smaller than the excitation wavelength.\textsuperscript{21} In a formal sense excitation of the dipolar surface plasmon, which results in SERS, takes place whenever there is a resonance as the denominators of $g$ and $g_0$ become small. This happens whenever $m_0$ and $m$ (refractive index of the particle for the arriving and reflected radiation respectively) approach the value $\sqrt{\varepsilon_r}$. For silver, in water, resonance occurs at 382 nm and at this excitation wavelength (for particles of 5 nm in diameter) a SERS enhancement factor $G$ of $10^6$ is predicted.\textsuperscript{20}
It should be noted here that it is most common in the studies of SERS active substrates to have the molecules directly attached to the metal surface. The molecules are bound to a metallic nano-structure which is a section of a cluster formed by aggregation of metal nanoparticles. This can lead to the formation of “hot spots” within the colloid aggregate.

The application of SERS to cyclodextrin-functionalized macroscopic surfaces has been reported previously. However, there have been only very few reports on the SERS properties of nanoparticles functionalized with cyclodextrins and their supramolecular host-guest complexes or these assemblies formed on electrode surfaces. Cyclodextrins hosts give a very weak Raman signal intensity, a property common to most sugars due to the very small Raman scattering cross section of the molecules. Thus, in principle this allows the virtually selective observation of Raman active guest molecules with good scattering properties especially those in close proximity to the surface plasmon “hot spots”. These spots on the particles (size and strength of electromagnetic enhancement) are determined by the geometry of the metal surface and the effect on the Raman signature by the accessibility to the Raman active molecule to this part of the metal surface.

5.2 Aim of this chapter

In this chapter we apply the SERS effect to probe the interaction between nanoparticles of different nature (Au, Pt) conveniently functionalized with TCD as hosts for compounds that can be used for the study of photoinduced hydrogen evolution. The inclusion of the guests into the β-CD cavity on the metal surface can result in a strong interaction of the guests and the incident/outgoing light and the surface plasmon band of the metal particles. An example for such an assembly is shown in figure 5.2 where gold nanoparticles and ada-MV are allowed to self-assemble in aqueous medium.

As a first approach we expect the vibrational modes corresponding to the adamantane functionality to be the most affected due to the inclusion. The passing from a freely vibrating molecule to a constrained environment within the CD cavity should give rise to changes in the vibrational spectra of this compound and translated into shifts in peak
positions (change in dielectric constant of the medium) as well as appearance/disappearance of bands (change of local symmetry, enhancement effect of previously weak bands). The assembly of this system is schematically represented in figure 5.2.

Figure 5.2. Example of one of the systems studied. Displayed are gold nanoparticles (ca. 30 nm diameter) stabilized with per-6-thiolated beta-cyclodextrin (TCD), and adamantane functionalized viologen (ada-MV). The small arrows on the adamantane indicate vibrational modes in the molecule that can be altered upon inclusion in the host.

5.3 Experimental

General procedures

The synthesis of the compounds TCD, Ru-bph and ada-MV are described in Chapter 2. All Raman measurements were carried out on silicon wafer washed thoroughly with acetone, water/acetone mixtures and finally with water and allowed to air dry. All solutions prepared in milli-Q grade water.

The smaller platinum nanoparticles were synthesized according to the procedure described by Kaifer28 (see Chapter 2). Platinum and gold nanoparticles of larger size (average diameter 30 nm) were purchased from Meliorum. The commercial nanoparticles (Pt and Au) are stabilized with ammonium salts and were delivered in aqueous solution (1 mg/ml concentration). The ammonium salts were exchanged with TCD, stabilizing the
particles through metal-sulphur bonds (more favorable than ammonium) and following the described procedure below.

*Exchange of the stabilizer for the large metal nanoparticles*

The solution of gold or platinum nanoparticles (20 ml of 1 mg/ml concentration) was mixed with 2.5 ml of a suspension of 1 mg/ml of TCD in water and stirred overnight at rt. The color of the gold colloid remained unchanged (purple) after the addition of the sulfur functionalized cyclodextrin. The deep purple color for this colloid is in general indication of a big particle size (tens of nanometers). It is also observed in the direct synthesis of gold colloid stabilized with TCD. On the other hand the platinum nanoparticles did show a color change during stabilizer exchange from grey to dark brown (typical for platinum colloids), the same color is observed for the direct synthesis of the platinum colloid (see Chapter 2). Color changes in metal particle colloids are generally ascribed to a change in particle morphology and size due to the adsorption of a molecule onto the particle surface. The change of color can be assigned to a shift in the position of the surface plasmon band in the order of a few nanometers. The nanoparticles were collected by centrifugation (5 min 15000 rpm). The nanoparticle pellet was re-suspended in DMF (HPLC grade) and isolated again through centrifugation (3 times) to remove the excess TCD. Then, with the same procedure they were washed with water to remove the DMF (3 times). Finally the nanoparticles were re-suspended in the minimum amount of water.
Chapter 5

Characterization of the nanoparticles with HR-TEM

Figure 5.3. HR-TEM images of the large Au nanoparticles stabilized with ammonium salts. The images show the polycrystalline structure of the colloidal particles and a relatively broad size distribution.

Figure 5.4. HR-TEM images of the large platinum nanoparticles stabilized with ammonium salts. The images show that the particles appear as several 100 nm sized clusters in solution rather than individual entities.
Figure 5.5. Platinum nanoparticles stabilized with TCD synthesized according to Kaifer et al. The left picture shows a detail with a scale bar that shows an average diameter for the particles of 1.5-2.5 nm.

Characterization of the different particles with HR-TEM is shown in figures 5.3-5.5. In the presence of the guest molecules the colloidal particles are not stable in solution and precipitate within minutes. A possible explanation of this can be the formation of particles aggregates connected by the guests\textsuperscript{10,29}.

Figure 5.6. Agglomerates of platinum particles stabilized with TCD and Ru-bph were found on the carbon foil. Part of such an agglomerate is seen in 5.6 left. In figure 5.6 right HR-TEM images were taken, Pt lattice spacings can be seen. The 2.27 Å \{111\} plane distance of Pt is seen often.
In a mixture of the colloidal particles with the ada-MV and Ru-bph guests described, a brown precipitate formed that could be re-suspended into solution by agitation. The brown precipitate can be isolated and characterized with HRTEM microscopy. The images show that the particles in the colloid do not coalesce or form bulk platinum but maintain their individual character, figure 5.6.

In a control experiment where cyclodextrin stabilized nanoparticles were used and Ru(bpy)$_3^{2+}$ was added the precipitation was also observed. However in this case longer time was needed for the precipitation to occur (hours). The aggregation process can be understood as a destabilization of the colloid due to the presence of the added molecules. This destabilization is induced by the neutralization of the electrostatic repulsive (negative) forces between the particles that keeps them from aggregating in the original solution. In the presence of the positively charged molecules the negatively charged surface of the metal is neutralized taking the particles out of solution. In the case of the cyclodextrin guests this precipitation should occur faster because of the inclusion in the cavity.

**Figure 5.7.** EDS is shown of one of the agglomerates of platinum particles stabilized with TCD and Ru-bph found on the carbon foil, showing Pt as the major signal. The Cu signal is caused by the Cu grid.

EDS (Energy Dispersive Spectroscopy) of the agglomerates found on the carbon covered copper grid clearly shows the presence of platinum from the colloidal metal particles. Signals corresponding to the sulfur can also be observed. Indication of ruthenium present in the sample is also observed however the signals are weak and long measuring times did not improve the signal to noise ratio, this probably due to the small concentration of...
Cyclodextrin Systems Studied with Raman Spectroscopy

ruthenium complex in relation to the amount of platinum or copper present in the sample measured, figure 5.7.

5.4. Results and Discussion

IR vibrational spectra of the viologen compounds

In figure 5.8 are shown the FTIR spectra recorded for the used viologens in KBr pellets.

![FTIR spectra](image)

**Figure 5.8.** IR vibrational spectra of *ada-MV* (dashed line) and *MV* (straight line) in KBr pellet.

Around 3500 cm\(^{-1}\) we observe a very broad band corresponding to the water molecules present in the sample probably from crystallization water. At 3000 cm\(^{-1}\) characteristic bands for C-H modes are present, at 812 cm\(^{-1}\) the out of plane bending for the same bond has a signal or for 4-substituted pyridines. The strong band centered at 1635 cm\(^{-1}\) corresponds to the C=C double bond stretching in an aromatic ring and is common of course in both compounds.

Both spectra show clear differences in several parts of the spectrum. The band corresponding to the C-H vibrations at 3000 cm\(^{-1}\) appears to have two separated sub-bands in the adamantane compound probably due to the existence of two kinds of C-H bonds (one from the methylene groups of the adamantane and one from the ternary
carbon). At 1454 cm\(^{-1}\) the ada-MV compound also presents a relatively much stronger band not present in the methylviologen.

**IR vibrational spectra of the stabilizer and colloid**

The spectra shown in figure 5.9 correspond to the IR spectra of TCD and platinum colloid stabilized with TCD. By comparison of the two spectra it is clear that both show very similar vibrational features indicating close interaction of the two components. The disappearance of the \(\text{–SH} \) vibrational mode at ca 2500 cm\(^{-1}\) shows the attachment of the stabilizer to the surface of the metal particles by formation of a \(\text{–S-Pt} \) bond.

**Figure 5.9.** IR vibrational spectra of the perthiolated cyclodextrin TCD (dashed line) and the platinum nano-particles stabilized with TCD (solid line). The arrow shows the band corresponding the \(\text{SH} \) vibrational mode.
5.4.2. Raman vibrational spectra of the studied compounds

The free TCD stabilizing molecule and attached on the platinum nanoparticles

The cyclodextrin with the seven SH groups on the primary side was studied in solution and solid state. As described in the literature, the measurements in solution show no Raman spectrum due to the bad Raman scattering properties of the cyclodextrin constituting glucose units. The solid state spectrum is shown in Fig. 5.10. Excitation wavelength was 632 nm.

![Figure 5.10. Raman spectrum of the TCD stabilizing molecule. Cyclodextrin measured in solid state with laser excitation at 632 nm. The SH band can be seen clearly at 2570 cm⁻¹.](image)

The spectrum was recorded after long measuring times (8 hours). These measuring conditions gave a well resolved spectrum with a high signal to noise ratio allowing us to compare our signatures to published spectra. This very long measuring time is atypical for Raman spectroscopy where spectra are usually recorded in shorter times. The 498 cm⁻¹ band is located close to a strong unassigned band of cyclodextrins and their derivatives. Most fingerprint bands are comparatively broad, whereas a sharp C-S stretching band appears at 725 cm⁻¹. At 2570 cm⁻¹ we can see the stretching for the SH vibration. Just below 3000 cm⁻¹ we observe a relatively broader band with three defined peaks characteristic for Raman signatures of sugar molecules.
The measurement of the platinum nanoparticles in aqueous solution lead to no recognizable Raman signature for the cyclodextrin stabilizer. The literature describes platinum nanoparticles as Raman substrates and gives a critical diameter value to observe surface enhancement effects when the size is at least 15 nm in diameter. In our case the nanoparticles employed had a diameter far below this critical value (average 1.5-2.5 nm) to observe a significant surface enhancement effect. The small platinum nanoparticles were thus measured in the solid state.

Figure 5.11. The solid line shows the Raman spectrum of solid (powdered) small platinum/TCD nanoparticles with excitation at 632 nm, the dashed line shows the spectrum of the TCD stabilizing molecule (see figure 5.10 for the complete spectrum). The sample was ground in an agatha mortar prior to measurement.

Around 700 cm⁻¹ a strong band can be observed that we ascribe to the C-S bond enhanced. The S-H band is not observed anymore indicating the attachment of the TCD to the surface of the metal. The appearance of a single C-S stretching band at a position typical for aliphatic thiols in the trans conformation shows that the sulfur groups are attached in a uniform conformation.
Raman spectra of the viologen compounds

The Raman spectra of the viologens were recorded in aqueous solution with laser excitation at 632 nm in some cases in the presence of a co-solvent such as acetonitrile (ca. 10%) to favor the solubility. Figure 5.12 shows the Raman signatures of the ada-MV used in the complexation experiments and the MV used as control compound, this spectrum is in excellent agreement with the literature. The spectrum corresponding to the ada-MV is shifted upwards for better comparison. Both signatures are very similar except for some differences that arise for bands of medium intensity around 800 and 1100 cm\(^{-1}\) that we assigned to the adamantane tail of the ada-MV.

The exact positions of these bands lie at 742, 775, 822, 1103 and 1121 cm\(^{-1}\) and these peaks are not present in the spectra of MV. At 840 cm\(^{-1}\) the MV shows a strong band that
can be assigned to a C-N or a C-C vibrational modes and has only a weaker character in the ada-MV. We also observe at 1200 cm$^{-1}$ the MV compound shows a band that has been assigned to the stretching of the N$^+$-CH$_3$ bond. In the adamantyl-viologen compound this band is relatively weak. Asymmetrically substituted viologens have shown to behave rather similar to symmetrical viologens according to their Raman signatures.38 This means that there should not be big differences between the spectra of the two compounds. The differences that appear in the bands at 840 and 1200 cm$^{-1}$ can be ascribed to a Fermi resonance. This effect is produced by overlap of overtones of vibrational modes (relatively weaker) of the molecule with other vibrational modes (relatively strong). The result is a splitting of the original bands into two bands of intermediate intensity. This occurs whenever two different vibrational states of a molecule transform according to the same irreducible representation of the molecular point group and have almost the same energy.39

Raman spectra of the ruthenium complexes

The ruthenium complexes were measured with laser light excitation at 458 nm in aqueous solution. This excitation lies close to the maximum of the $^1$MLCT absorption of the ruthenium chromophore. When a molecule is excited at a wavelength in resonance with its electronic absorption spectrum a strong resonance Raman effect (RR) is expected. Resonance Raman spectroscopy takes advantage of this effect by adjusting the energy of the incoming laser pulse to coincide with an electronic transition of the measured molecule. Once the molecule is excited in one electronic transition (resonance) the vibrational modes associated with that transition exhibit greater Raman scattering intensity. This effect usually overwhelms all other Raman signals from other transitions not “excited” by the resonant light. In the case of chromophores with charge transfer transitions resonance Raman generally enhances metal to ligand stretching modes. In the case of the ruthenium complexes we are most probably observing the Raman signature of the formally reduced bipyridine and in the case of the functionalized compound we are looking at the reduced biphenyl-bipyridine.25, 26
In our case the compounds gave intense and sharp signals only after applying long measuring times (average time 3 hours per spectrum). The measurement was set to reduce the background noise in the spectrum with the inconvenience of very long measuring times. In comparison to shorter measuring times the S/N ratio increases significantly, figure 5.13.

**Figure 5.13** Raman signatures for the ruthenium guest Ru(bph) \( \cdots \) and Ru(bpy)\( _2^{2+} \) \( \cdots \) used as control compound for the measurements. Clear differences between the two compounds are present.

Figure 5.13 shows the Raman signatures for the Ru(bph) guest and Ru(bpy)\( _2^{2+} \) used as control compound. The assignments of vibrational bands were made tentatively by comparison with reported results for related compounds\(^{40}\). The spectrum for the parent compound Ru(bpy)\( _2^{2+} \) corresponds perfectly with the spectra published in the literature.\(^{41}\)  
This spectrum also surprises because of the similarity to bipyridine Raman spectra absorbed on gold electrodes at negatives potentials.\(^{45}\) This indicates that the Raman signature observed corresponds to the formally reduced bipyridine within the Ru(bpy)\( _2^{2+} \) complex after excitation at the \(^1\)MLCT band after a formal electron transfer form the metal to the ligand. Differences appear between 1200-1400 cm\(^{-1}\) and at 1500 cm\(^{-1}\). At these wavenumbers Ru(bph) shows duplets where Ru(bpy)\( _2^{2+} \) shows only a single peak. The splitting of these bands into two bands is of course assigned to the introduction of the biphenyl tail. These new bands can be assigned to a splitting of a previously existing band due to Fermi resonance or assigned directly to new bands arising from the...
Chapter 5

substitution with the biphenyl tail. Within each duplet the bands show similar but overall reduced intensity when compared to the original singlet. This makes us assign the splitting of these bands to Fermi resonances by overlap of overtones of vibrational modes of the biphenyl tail with vibrational modes of the reduced bipyridine. Except for the Fermi resonances above 1400 cm\(^{-1}\) both complexes show similar signatures with features, that have been assigned in the literature\(^{42,43}\) to 4,4'-bipyridine adsorbed on a gold or silver surface before.

5.4.3 Host-guest interaction on MNP surface studied with SERS

*Host-guest interaction studied with SERS between ada-MV and TCD functionalized MNP*

Some authors have described how the direct excitation of the surface plasmon of metal particles can be favorable in order to enhance the SERS effect. The theoretical value for the platinum surface plasmon band has been predicted to be at 215 nm\(^{44}\). This band appears for gold colloids in the visible part of the spectrum making the direct excitation of the plasmon more accessible with common laser excitation wavelengths (532 or 633 nm). However, we expected to be able to extend the results observed on the gold nanoparticles to platinum. We believe that similar supramolecular interactions can occur on the metal nano-particles independently of the nature of the metal.

Figure 5.14 shows the Raman spectra of the ada-MV compound alone (A) and in the presence of gold and platinum MNP (B and C respectively) all with non-resonant laser excitation at 632 nm. The samples where measured as aqueous solutions (5 % acetonitrile as co-solvent can be present to favor solubility and complexation). The MNP diameter lies around 30 nm and the stabilizing agent was TCD. The concentration of ada-MV was kept constant in all three spectra shown (~ 5 x 10\(^{-4}\) M). Spectrum A and C show the normal Raman signature for the ada-MV compound indicating no interaction. Spectrum B (in the presence of the Au-TCD MNP) showed however many new intense bands at new peak positions as well as bands that overlap with the original peaks corresponding to the ada-MV alone.
Figure 5.14. Raman spectra of ada-MV in the absence (A) and presence (B for gold and C for platinum) of MNP-TCD with non-resonant laser excitation at 632 nm.

The assignment of the new bands is not straightforward since the extent of SERS enhancement depends not only on distance but also on the degree of communication between the adsorbate and substrate and the effect may not be uniform across the entire spectrum. Despite the challenges of formally assigning each vibrational mode, it is clear that the ada-MV interacts with the cyclodextrin cavity immobilized on the surface of the particle.

As a control, similar experiments were performed with methyl-viologen. The Raman spectra of MV and its different redox forms have been well documented and there is excellent agreement between these previous reports and the spectra reported here. Figure 5.15 shows the normal Raman spectrum of MV and the mixture of MV with the Pt and Au MNP stabilized with TCD. Figure 5.15 shows that the presence of cyclodextrin functionalized gold or platinum nanoparticles does not change the Raman signature of the MV as significantly as that found for the adamantyl derivative. However, upon closer inspection a slight increase in the 1400-1500 cm\(^{-1}\) region can be observed for the mixture with the gold MNPs.
(spectrum E). This substantially weaker change is in principle in agreement with the much weaker binding of methyl-viologen (or “un-substituted” viologens) to the β-cyclodextrin cavity. The concentration of MV was kept constant in all three spectra shown (~ 5 x 10^{-4} M).

Figure 5.15. Raman spectra of MV (D) in aqueous solution and in the presence of the Au or Pt MNP stabilized with TCD (E and F respectively) after non resonant laser excitation at 632 nm.

In a deeper analysis of the spectra we searched to study the real effect of the proximity of the ada-MV compound to the surface of the MNPs. Figure 5.16 shows the comparison of the spectra recorded for the mixtures of ada-MV and MV with the Au MNPs. From the spectrum of the mixture of MV with the Au MNPs we subtracted the corresponding strong contribution of Raman signature coming from the MV alone in aqueous solution. The result is the dashed spectrum shown in figure 5.16. Qualitatively the new bands observed for the mixture of ada-MV and Au MNPs can also be observed with similar shape and position indicating some interaction of the viologen MV with the cyclodextrin cavity. However it is clearly visible that even if the MV is bound or in close proximity to the MNP, for the ada-MV bound to the MNP the quality of the spectrum and the intensity of the peaks are very different.
As discussed before, we believe that it is very likely that the interactions between the functionalized particles and the viologen guest molecules are occurring for the gold and the platinum particles. However, clearly they are not observed for the platinum particles, since as discussed, these particles have no suitable properties as SERS substrates.

Host-guest interaction studied with SERS between Rubph and TCD functionalized MNP

Similar experiments were performed with a ruthenium complex that contains a biphenyl substituent as a guest moiety, using ruthenium trisbipyridyl as the reference compound (figure 5.17). In these conditions, no changes in the resonant Raman signatures could be observed. In all cases the concentration of ruthenium complex was kept constant (about $10^{-4}$ M).

Figure 5.16. Comparison of the SERS effect on the ada-MV and the MV sample mixed with the Au MNPs (the contribution of the free MV was subtracted using spectrum D in figure 5.15). The dashed spectrum is shifted upwards for clarity.
Apparently, the biphenyl unit is unable to give good complexation with the cyclodextrin when the latter is attached to a surface. It is possible that immobilization on the nanoparticle results in the cyclodextrin cavity having a substantial smaller penetration depth. This reduces the binding strength of the cavity towards relatively “longer” guests that need this complementarity for an appropriate host-guest interaction.

It is also important to note that the SERS effect is normally observed following strong physisorption or chemisorption of the analyte (e.g. pyridine) onto aggregated silver colloids. In contrast, here a not completely aggregated functionalized gold nanoparticle in aqueous solution is used. Moreover, the analyte is interacting with the cyclodextrin stabilizer of the nanoparticle through host-guest complex formation based on weak hydrophobic interactions and does not bind directly to the metal surface of the particle.
Figure 5.18. Control experiment corresponding to the studies carried out on the ruthenium complex $\text{Ru(bpy)}_3^{2+}$ with resonant excitation at 458 nm.

Figure 5.18 shows the spectra of $\text{Ru(bpy)}_3^{2+}$ in aqueous solution and in the presence of the gold and platinum MNPs, in all three cases the concentration was kept constant. All three spectra are nearly identical except for the intensity that decreases when the concentration of nano-particles increases. To have a better insight also the peak positions corresponding to bands related to the biphenyl tail were analyzed more carefully. The position of the peaks corresponding to this part of the molecule did not show major variations and the peaks only shifted within the experimental error.

5.5 Conclusions

In the experiments where the ruthenium guest with the biphenyl tail was used we did not observe a significant change in the Raman signatures between the compound alone and the compound in the presence of the platinum or gold TCD nano-particles. We observed dramatic changes in the Raman spectrum only in case of a guest with an adamantane as binding tail and with gold as a substrate. This is most probably due to the
stronger cyclodextrin interaction of the adamantane compared to the biphenyl and the known qualities of gold as a substrate for SERS when compared to platinum.

We can conclude that we have been unable to attain the ideal conditions in which a good comparison can be made between individual decorated functionalized particles (e.g. ada-MV/Au-TCD) and particles where no supramolecular interaction is present (e.g. MV/Au-TCD). Clearly the clustering of the platinum-TCD nano-particles occurs with the guests and with the reference molecules. In this clustered material "hot spots" can be generated where the SERS effect is strongest and in both cases (MV and ada-MV) new signals emerge. There is however no specific signature of the guest moiety that is clearly enhanced. The new signals can be attributed to MV and ada-MV molecules that are present within the clustered metal particles, and vibrations over the entire molecule are enhanced.

Clearly, a correlation should be present between the amount of clustering or the cluster size and the newly emerged signals. In order to get a better grip of these effects, dynamic light scattering could be combined with the SERS measurement.

It would be preferable however to obtain conditions in which clustering does not occur, so that individual particles and their interaction with guest molecules can be studied. It has to be realized that clustering of metal nano-particles upon addition of ions or molecules is an often encountered phenomenon.

The indication of non-covalent interaction of substances in aqueous solution with metal nano-surfaces with interesting catalytic properties, opens the possibility of future studies in this direction.

Work is currently in progress to compare the described results using gold nano-rods, instead of particles, since it is known that the shape of nano-structure plays a determining role. Using thus the same components and assemblies presented here we should be able to render a final and clear answer to the open questions remaining here.
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Chapter 5


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168
Cyclodextrin Systems Studied with Raman Spectroscopy


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