Raman Spectroscopy

DOI: 10.1002/ange.201407642

Enantioselective Discrimination of Alcohols by Hydrogen Bonding: A SERS Study**

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Abstract: *Efficient and generic enantioselective discrimination of various chiral alcohols is achieved by using surface-enhanced Raman scattering (SERS) spectroscopy through charge–transfer (CT) contributions. The relative intensities of the peaks in the SERS spectra of a chiral selector are strongly dependent on the chirality of its surroundings. This highly distinct spectral discrepancy may be due to the tendency of chiral isomers to form intermolecular hydrogen-bonding complexes with the chiral selector in different molecular orientations, resulting in different CT states and SERS intensities of the adsorbates in the system. This study opens a new avenue leading to the development of novel enantiosensing strategies. A particular advantage of this approach is that it is label-free and does not employ any chiral reagents, including chiral light.*

Molecular chirality is a prominent characteristic of biological processes, and enantiomers of a chiral molecule may exhibit striking differences in terms of physiological responses.[1–3] The exploitation of techniques to discriminate between enantiomers is critical in various fields of science and technology, such as catalytic chemistry, biotechnology, and especially pharmaceutical science.[4] Considerable efforts have been devoted to the development of specific chiral selectors and interfaces that enable enantioselective discrimination by vibrational circular dichroism (VCD),[5] UV/Vis,[6] fluorescence,[7] Raman optical activity (ROA),[8] and NMR spectroscopy.[9] However, most of these techniques are time-consuming, can only be used with specialized chiral selectors, and require complicated syntheses and pretreatment steps. Therefore, there is an urgent need for the development of a simple, generic, and efficient technique to realize enantioselective discrimination.

Surface-enhanced Raman scattering (SERS), which affords single-molecule sensitivity and molecular specificity, has emerged as a powerful technique for monitoring selective recognition, especially in the fields of biodetection, surface science, and environmental analysis.[10–13] The tremendous enhancement of SERS signals arises mainly from two mechanisms: electromagnetic (EM) and charge–transfer (CT) effects.[14–19] Unlike EM enhancement,[14,15] which stems from localized surface plasmon resonance on a metal substrate, CT enhancement[16,17] is a resonance-like process in which the CT resonance depends on the energy difference between the Fermi level of a metal substrate and the molecular orbital of an adsorbate. When the energy of the laser excitation matches this energy difference, a favorable CT state may be generated, and the CT resonance process occurs.[16–19] SERS retains the rich chemical and structural information afforded by Raman spectroscopy and produces refined fingerprint vibrational spectra,[15,20] so that it can respond to the effects of intermolecular interactions on the surroundings.[21–23] Thus far, there have been few precedents for chiral discrimination by SERS, and they have used specific chiral molecules as selectors to obtain discernible spectra between the enantiomers of a chiral molecule, but suffered from a lack of generality and poor distinction between enantiomers.[24,25] However, generic spectroscopic enantioselective detection by SERS has not been realized owing to the difficulties in the fabrication of a SERS receptor with the specific stereochemical properties required to detect molecular chirality. Therefore, devising a simple and efficient SERS technique to differentiate between enantiomers of chiral molecules remains a challenge.

It is widely accepted that SERS is sensitive to variations in the molecular environment, such as temperature,[26] pH,[27] laser energy,[28] intermolecular hydrogen bonding,[29] and substrate arrays.[30] Changes in the relative Raman intensities of the adsorbates in a SERS spectrum could be a visible manifestation of a CT transition and be considered as a propensity rule to estimate the occurrence of a photo-induced CT process.[16,19,31] Such behavior in a SERS spectrum should be observed even if the adsorbed probe molecule interacts with the two enantiomers of a chiral molecule, because vibrational modes of adsorbates vary in response to their environment in order to modulate the minimum interfacial free energy,[32] which is a direct reflection of the modification of the molecular electronic structure. Therefore,

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[**] This research was supported by the National Natural Science Foundation (21273091, 21221063, and 21327803) of China, the Specialized Research Fund for the Doctoral Program of Higher Education (20110061110017), the 111 project (B06009), and the Development Program of the Science and Technology of Jilin Province (20110338, 20130305005GX). SERS = Surface-enhanced Raman scattering.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201407642.

if SERS based on the CT contribution (CT-SERS) can discriminate chirality, the characteristic SERS spectrum should ultimately be different for two enantiomeric liquids as a difference exists in the stereoscopic configuration of the intermolecular hydrogen bonds between the two enantiomers and the chiral selector. Herein, we present, for the first time, a reliable and simple method for enantioselective discrimination by SERS spectroscopy that makes use of intermolecular hydrogen bonding and CT contributions and does not require the sophisticated manufacture of a specialized chiral selector. Our work demonstrates the significance of the CT contribution in enantioselective discrimination by SERS, aside from the universal EM enhancement, which is based on the excitation of localized surface plasmons. Moreover, a particular significance of the proposed approach is that it is label-free and does not employ any chiral reagents, including chiral light, as is the case for ROA spectroscopy.

On the basis of these considerations, we envisioned that the stereoisomerism of enantiomers in CT-SERS may be exploited for enantioselective discrimination by using a complex consisting of silver nanoparticles and *para*-mercaptopyridine (Ag–MPY NPs) covalently bonded by S–Ag bonds (Figure 1; for details, see the Supporting Information). The

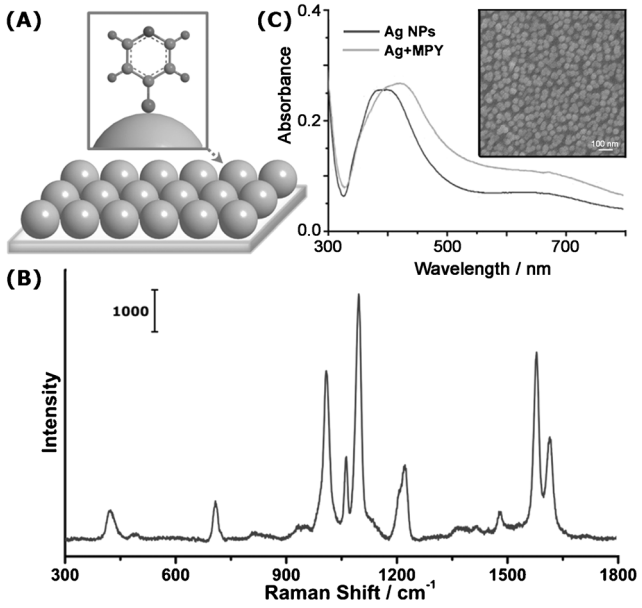

Figure 1. A) Ag–MPY complex deposited on a glass substrate. B) SERS spectrum of MPY in the complex. C) UV/Vis absorption spectra of films of assembled Ag NPs and the Ag–MPY complex. A representative SEM image of the assembled Ag NPs film is also shown.

probe molecule, MPY, has aroused particular interest owing to its unique SERS signals and characteristic features, which are significant for revealing the molecular electronic structure of the metal-MPY complex.[33,34] After fabrication, the Ag–MPY complex was immersed in the same volume of various chiral molecules in their racemic and enantiomerically pure forms to measure SERS directly without withdrawing the complex from the liquid.

The SERS spectra of the Ag–MPY complexes were measured using a Horiba LabRAM HR-800 Raman spectrophotometer equipped with a 514 nm Ar ion laser. Several intense SERS features that are characteristic of the MPY molecule were observed[34–36] (Figure 1 A), such as bands at 1009 cm^{-1} (ascribed to the ring breathing ($1a_1$) mode), 1096 cm^{-1} (ring breathing ($12a_1$) coupled with ν(C–S) modes), 1578 cm^{-1} (ν(C–C) with deprotonated nitrogen, $8b_2$ mode), and at 1612 cm^{-1} (ν(C–C) with protonated nitrogen, $8a_1$ mode; for the band assignments of MPY, see the Supporting Information, Table S1).[34,36] Upon exposure of the Ag–MPY complex to 1,1,1-trifluoro-2-propanol (TFIP), a distinct re-shaping of the SERS spectral profile occurred, and a new band corresponding to TFIP appeared at 795 cm^{-1}. The relative intensities of several pairs of bands were inversed (Figure 2 A); namely, the relative intensities of the following

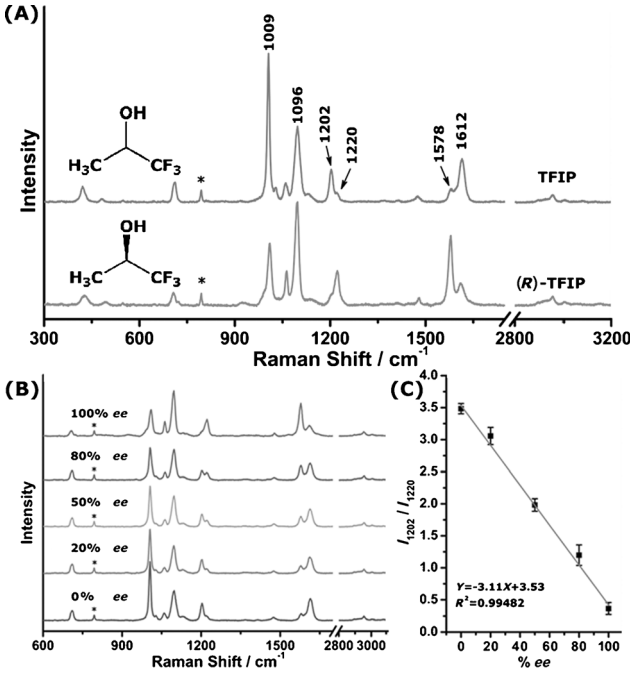

Figure 2. A) Normalized SERS spectra of the Ag–MPY complex upon exposure to racemic TFIP and (*R*)-TFIP, respectively. B) Normalized SERS spectra of the Ag–MPY complex in the presence of TFIP with various *ee* values. C) Correlation between the differences in the relative intensity ratio of I_{1202}/I_{1220} and the *ee* values (in %). All of the Raman peaks were normalized to the intensity of the band at 795 cm^{-1}, which was assigned to TFIP (marked with an asterisk in the figure).

pairs of bands were inversed: 1009 cm^{-1}/1096 cm^{-1}, 1202 cm^{-1}/1220 cm^{-1}, and 1578 cm^{-1}/1612 cm^{-1}. For the S-bonded Ag–MPY complex, the X-sensitive mode at 1096 cm^{-1}, assigned to the ring-breathing coupled with the ν(C–S) mode, which originates from a strong combination between the substitute and the aromatic ring mode and is extremely sensitive to the local environment, can be considered as an indicator. It is not surprising that the relative intensity of the band at 1096 cm^{-1} strongly diminishes owing to the formation of strong intermolecular hydrogen bonds between MPY and TFIP, as the X-sensitive modes are

sensitive to the local environment and always serve as a spectral characteristic of MPY.[34,36,37] It has been reported that the terminal N atom of MPY easily forms a hydrogen bond with an alcohol hydroxy group[38,39] as a result of its strong hydrogen-bond basicity. This hydrogen bonding interaction between the N atom and the hydroxy group may play a dominant role in the present intermolecular hydrogen bonds in addition to other kinds of interactions in the system, such as CH–π interactions.[40] Furthermore, the intensification of the bands at 1202 cm^{-1}, ascribed to β(CH) ($9a_1$)/δ(NH) modes, and 1612 cm^{-1}, attributed to ν(CC) (with protonated nitrogen, $8a_1$ mode),[36] could indicate the formation of a hydrogen bond between the N atom of MPY and the hydroxy group of TFIP.

However, the dramatic change in the SERS profile when the Ag–MPY complex was immersed in only one of the enantiomers of TFIP [(*R*)-TFIP; Figure 2A] is remarkable. In this case, the SERS spectrum of MPY is consistent with the profiles measured in other achiral fluorine-containing or fluorine-free alcohols (Figure S1). It is believed that these dramatic changes in the relative intensities in the SERS spectrum of MPY result from the difference in stereoscopic configuration between the two enantiomers and MPY, that is, the *S* enantiomer [(*S*)-TFIP], forming a more favorable configuration of intermolecular hydrogen bonds, is more likely to be selectively distinguished. In the recognition process, the *S* enantiomer may show unique intermolecular hydrogen bonding interactions with MPY in comparison to the *R* enantiomer, resulting in a more energetically favorable interaction. In fact, it has been reported that the strong directionality of the dipole moment of the hydroxy group of TFIP affords a strong chiral discrimination effect.[41] This spectral change is quite reasonable if the MPY molecules recognize the *S* enantiomers in a racemic mixture as a result of an attractive interaction mainly between the hydroxy group and the terminal N atom. Therefore, this explains why a phenylthiol molecule without a terminal N atom cannot be utilized for the discrimination of the two enantiomers of TFIP (Figure S2). Taking into account that the enantioselective discrimination in our technique was essentially due to the formation of noncovalent hydrogen bonds, the reversible change in the spectrum caused by the presence or absence of the racemic liquid can be understood (Figure S3).

To examine the efficacy of the enantioselective discrimination, the enantiomeric purity of TFIP with various *ee* values was studied (Figure 2B). All of the SERS spectra were normalized to the intensity of the band at 795 cm^{-1}, attributed to TFIP. It was observed that the relative intensities of some peaks in the SERS spectra of MPY depend on the *ee* value of the TFIP mixture. The pair of bands at 1202 and 1220 cm^{-1} was chosen as an indicator, as the peak at 1202 cm^{-1}, which was assigned to the β(CH)/δ(NH) modes, can be regarded as a direct response to the enantioselectivity through the formation of hydrogen bonds between MPY and the chiral alcohol. Surprisingly, plotting the difference in the ratio of the relative intensities of the peaks at 1202/1220 cm^{-1} against the *ee* value (in %) revealed a linear correlation with a coefficient of $R^2 = 0.9948$ (Figure 2C). It is evident that our Ag–MPY system is capable of enantioselective discrimination. This is the first demonstration that an achiral system can determine enantiomeric purity by using SERS spectroscopy.

Furthermore, it is worth mentioning that our approach constitutes a universally applicable method for discriminating the enantiomers of various kinds of alcohols. The optically pure and racemic forms of two other chiral alcohols, 2-butanol and 1-methoxy-2-propanol (MOIP), were chosen to verify the reliability of this system as depicted in Figure 3. All of the SERS band intensities were normalized with respect to the absolute intensity of the solvent peaks at 821 and 855 cm^{-1}, respectively. It was obvious that the aforementioned bands varied similarly to the SERS spectra of the Ag–MPY complex in TFIP, despite their greatly diminished magnitudes (Figure 3A and D). Even for the ring-breathing and the X-sensitive modes of MPY, a similar tendency of intensity

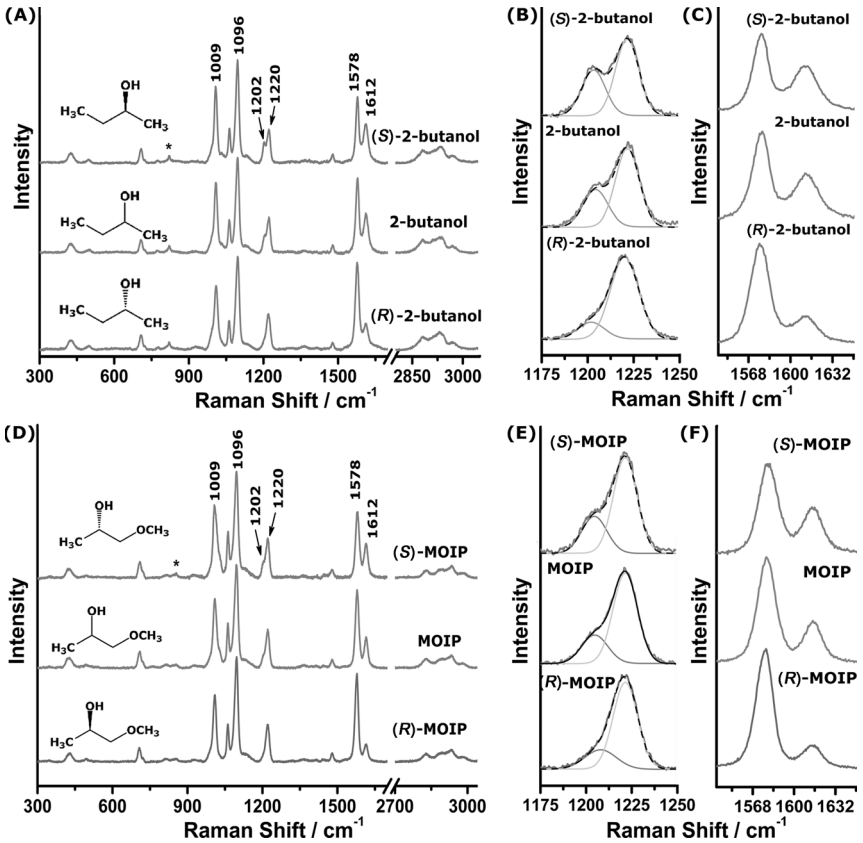

Figure 3. A) and D) Normalized SERS spectra of the MPY–Ag complex separately immersed in different chiral alcohols (2-butanol and MOIP, respectively) in their optically pure and racemic forms. B, E) and C, F) Enlargements of the 1175–1250 cm^{-1} and 1540–1650 cm^{-1} spectral regions of the SERS spectra shown in (A) and (D), respectively.

changes could be observed. As fluorine is the most electronegative element, the trifluoromethyl group in a TFIP molecule has strongly electron-withdrawing properties. Thus, the hydroxy group in TFIP has a greater tendency to form hydrogen bonds than those of 2-butanol and MOIP, which contain the less electronegative ethyl (CH_3CH_2) and methoxy (CH_3O) groups, respectively. In spite of this, a distinct decrease in the intensity of the band at 1578 cm^{-1} and a simultaneous increase in the intensity of the bands at 1612 cm^{-1} were observed when the Ag–MPY complex was immersed in a solution of the *S* enantiomer, or even in the racemic mixture (Figure 3C and F). Moreover, the enantioselective discrimination indicator, i.e., the ratio of the intensity of the bands at 1202 and 1220 cm^{-1}, in both 2-butanol and MOIP increased with an increase in the *S* enantiomer content (Figure 3B and E).

The origin of the SERS enantioselective discrimination behavior of the adsorbed MPY molecules should be related to the protonation of the terminal N atom in the Ag–MPY complex when immersed in different enantiomers through hydrogen bonding interactions. This protonation causes an orientation difference between the two complexes of the two enantiomers and MPY relative to the silver surface, which could result in a distinct difference in the SERS spectra.[15,35] It is considered that there are some slight differences in the spatial structures of the *S* and *R* enantiomer–MPY complexes versus the Ag NPs, generating different energy states that could induce differentiated CT processes between the adsorbed MPY and the Ag substrate. In this chiral discrimination process, CT contributes to the amplification of very slight differences between the two complexes, leading to remarkable differences in the relative intensities in the SERS spectra. For a CT resonance process, it is expected that CT-SERS intensities correspond to suitable CT states of the metal–adsorbate complex.[28,42] Thus, a propensity rule can be empirically stated that the strong and selective enhancement of the non-totally symmetric (b_2) and totally symmetric (a_1) modes can be considered to be an indicator for the participation of a CT process in SERS spectra of molecules with C_{2v} symmetry.[16,18,42] In Figure 2A and Figure 3A and D, the enhancement of the a_1 modes, such as the ring-breathing mode at 1009 cm^{-1}, the ring-breathing/ν(CS) mode at 1096 cm^{-1}, the β(CH)/δ(NH) mode at 1202 cm^{-1}, and the ν(CC) mode at 1612 cm^{-1} ($8a_1$), occurs only upon immersion in the liquid containing the *S* enantiomer, whereas the b_2 mode at 1578 cm^{-1}, attributed to ν(CC) ($8b_2$), is diminished in comparison with the SERS spectrum of the pure Ag–MPY complex (Figure S4). Therefore, a CT process could be involved in the chiral discrimination process.

According to the CT mechanism, both Frank–Condon and Herzberg–Teller terms contribute to the enhancement of the a_1 modes, whereas the b_2 modes can only be enhanced through Herzberg–Teller terms.[35,42,43] The S-type enantioselective discrimination process in the system increases the contribution of the Frank–Condon term and simultaneously inhibits the Herzberg–Teller term. The inhibition is due to the hydrogen bonding interactions between the *S* enantiomer and MPY, resulting in vibronic coupling between two close CT states that is not favorable for a CT process, which further reduces the influence of the Herzberg–Teller contribution. Consequently, the intensity of the b_2 mode of MPY at 1578 cm^{-1} is reduced. Considering the reduction of the symmetry of the Ag–MPY complex, we can argue that the Frank–Condon factors dominate the enhanced CT-SERS intensities.[35,42] Nevertheless, the *R* enantiomer, in spite of hydrogen bonding, may have a different orientation caused by protonation that leads to some suitable CT state being involved in the CT transition. Thus, SERS enhancement of the MPY molecules may still be influenced by the Herzberg–Teller coupling, which causes the differences in spectral shape. Therefore, it may be concluded that the acquisition of enantioselective SERS spectra is dominated by the CT enhancement mechanism, which is influenced by the protonation of MPY through strong intermolecular hydrogen bonding in the system; the effect of this mechanism manifests itself in the tremendous differences in the SERS spectra. Whereas attenuated total reflectance infrared (ATR-IR) and normal Raman spectra (Figures S5–S7) cannot differentiate between the *R* and *S* enantiomers of the studied alcohols, CT-SERS spectroscopy is capable of discriminating enantiomers. As discussed above, complexes of the *S* enantiomer with MPY may show unique spatial orientation relative to the Ag surface in comparison with the complexes of the *R* enantiomer with MPY, leading to different energy states for the Ag–MPY complex and the occurrence of a unique CT process.

In summary, by taking advantage of charge-transfer contributions, SERS spectroscopy has been reported to be suitable for enantioselective discrimination for the first time. The selectivity originated from the enantioselectivity of the intermolecular hydrogen bonding interactions. The difference in the protonation of the Ag–MPY complex through hydrogen bonding led to the formation of different CT states of the Ag–MPY complex, which are involved in the CT process, and further manifested in a tremendous difference in the SERS spectra. In particular, the *ee* value can be determined by the ratio of the relative intensities in the region near 1200 cm^{-1}. These results provide important improvements in the field of label-free enantioselective discrimination without the employment of any chiral agents.

Received: July 26, 2014
Revised: September 2, 2014
Published online: October 10, 2014

Keywords: charge transfer · chiral recognition · hydrogen bonding · surface-enhanced Raman scattering

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