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# Elucidation of Interaction between Metal-Free Tetraphenylporphine and Surface Ag Atoms through Temporal Fluctuation of Surface-Enhanced Resonance Raman Scattering and Background-Light Emission

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We have observed simultaneously temporal fluctuation of surface-enhanced resonance Raman scattering (SERRS) and its background-light emission from single Ag nanoaggregates that were adsorbed with metal-free tetraphenylporphine ($H_2TPP$) molecules. We found that temporally stable SERRS spectra showed clearly a SERRS band that is attributed to a stretching mode of a chemical bond between a carbon atom and a non-hydrogenated nitrogen atom ($C_\alpha-N$). This stretching mode was not observed in regular resonance Raman spectra which are free from surface enhancement. On the other hand, we also found that temporally unstable SERRS spectra did not clearly show a $C_\alpha-N$ stretching mode in SERRS bands. Furthermore, temporally stable SERRS spectra were accompanied by temporally stable background-light emission. Kobayashi et al. [*J. Phys. Chem.* **1985**, *89*, 5174] reported that formation of an Ag−N bond between surface Ag atoms and non-hydrogenated N atoms in a pyrrole ring enhances the intensity of a $C_\alpha-N$ stretching mode. Thus, the observed relationship between clear appearance of a $C_\alpha-N$ stretching mode and temporal stability of SERRS plus background-light emission strongly suggests that formation of a stable Ag−N bond suppresses fluctuation of both SERRS and background-light emission. Furthermore, the observed relationship implies that chemical contribution to SERRS is stabilization of $H_2TPP$ molecules that are adsorbed on SERRS-active sites by formation of Ag−N bonds. Additionally, we attributed background-light emission to luminescence of complexes between $H_2TPP$ molecules and surface Ag atoms considering possible formation of Ag−N bonds, synchronized SERRS intensity with background-light emission intensity, blue-shifted background-light emission maxima from normal fluorescence maxima, and previous reports related to electronic structures of $H_2TPP$ molecules on Ag surfaces.

## Introduction

Surface-enhanced resonance Raman scattering (SERRS) is a highly sensitive tool for structural analysis of molecules that are adsorbed on a metal surface. Indeed, SERRS enables us to identify molecular vibrations even under the single-molecule level.[1−10] It is widely accepted that both electromagnetic (EM) and chemical mechanisms contribute to SERRS.[1−19] There is no doubt that EM fields that are coupled with plasmon mainly contribute to large enhancement of Raman scattering, because recent calculations of EM fields at interparticle junctions and at sharp edges of noble metal nanoaggregates well predict enhancement of Raman scattering by a factor of $10^8$ to $10^{14}$.[3,10] Furthermore, the relationship between strong SERRS intensity and Ag−nanoparticle microstructure/particle interactions was experimentally evidenced.[20−22] We have already identified that optimum polarization, spectral maxima, and Q factors of plasmon resonance are all essentials of large enhancement of Raman scattering.[16−19] However, only the EM mechanism cannot provide reasons why all kinds of molecules adsorbed on interparticle junctions and sharp edges do not always generate SERRS activities. For example, we do not observe an enhanced Raman signal of water even from Ag nanoaggregates in an aqueous solution. Such questions strongly motivate us to consider that chemical interaction between molecules and Ag surfaces contributes to a large enhancement of Raman scattering.[4,5,7,11−15,23,24] Thus, it is important to investigate chemical interaction between SERRS-active molecules and metal surfaces to explore a SERRS-chemical mechanism.

Several spectroscopic studies on SERRS-active molecules which have non-hydrogen-terminated N atoms showed that the N atoms interact with Ag surface atoms and form Ag−N chemical bonds. The formation of Ag−N chemical bonds is reasonable because the nitrogen lone pair has strong affinity to the Ag surface;[11] however, the Ag−N stretching mode is difficult to observe in SERRS spectra because of its low frequency of Raman shift ($\sim$250 or $\sim$350 cm$^{-1}$) and weak intensity.[13] From SERRS spectroscopy of $H_2TPP$ molecules adsorbed on Ag substrates, Itoh et al. identified that an Ag−N chemical bond in a pyrrole ring enhances a SERRS band of a $C_\alpha-N$ stretching mode.[25,26] Thus, we expected to observe chemical interaction between SERRS-active molecules and Ag

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surfaces through the observation of a $C_\alpha$−N stretching mode instead of an Ag−N stretching mode. Conventional ensemble spectroscopy of SERRS cannot directly reveal individual chemical interactions, thereby providing averaged information on many molecules interacting and not interacting with Ag surface atoms. Thus, it would be advantageous to attempt single-molecule SERRS spectroscopy to selectively investigate chemical interactions between $H_2TPP$ molecules and Ag surfaces.

In the current study, we applied time-resolved SERRS spectroscopy to the single Ag nanoaggregates on which $H_2$-TPP molecules are adsorbed to reveal chemical interaction between $H_2TPP$ molecules and Ag surfaces. We investigated temporal fluctuations of SERRS spectra and their background-light emission spectra. Background-light emission is not associated with normal Raman scattering and has been pointed out as an important characteristic of SERRS.[4,7,11−15,19] We found that both SERRS and background-light emission were temporally stable, which is not enhanced, when a $C_\alpha$−N stretching mode clearly appeared in SERRS spectra. This observation suggests that stable Ag−N chemical bonds suppress temporal fluctuations of both SERRS and background-light emission. The suppression of the temporal fluctuations by Ag−N bonds implies that the chemical contribution to SERRS is stabilization of adsorbed $H_2TPP$ molecules on SERRS-active sites by formation of Ag−N bonds. Additionally, we attributed background-light emission to luminescence from complexes of $H_2TPP$ molecules and surface Ag atoms in terms of several lines of evidence: formation of Ag−N bonds, simultaneous fluctuation of SERRS intensity with background-light emission intensity, background-light emission maxima blue shifted from the normal $H_2TPP$ fluorescence maxima, and previous work on electronic structures of $H_2TPP$ molecules on Ag surfaces.[27−29]

### Experimental Section

Metal-free 5,10,15,20-tetraphenylporphine ($H_2TPP$) (Aldrich, 99+%, Tokyo) was used as purchased. Colloidal silver nanoparticles were prepared in an aqueous solution following a literature method.[2] An extinction spectrum of the Ag colloidal solution used in the current work showed a single maximum at 410 nm (figure not shown), thus showing that the amount of aggregated colloidal particles was negligible in the initial solution. SERRS-active Ag particles were prepared by mixing a $H_2TPP$ aqueous solution ($1.8 \times 10^{-7}$ M), a NaCl aqueous solution (10 mM), and an Ag colloidal solution ($1.0 \times 10^{-10}$ M). At first, a $H_2TPP$ solution at a higher concentration ($6.0 \times 10^{-5}$ M) was prepared in acetone, then repeatedly diluted with water to a $4.0 \times 10^{-5}$ M solution and a $1.8 \times 10^{-7}$ M solution. Care was taken for minimizing aggregation of $H_2TPP$. An aliquot of the mixture was spin-coated on a glass plate after a 30-min incubation at room temperature (17 °C). The Ag particles on the glass plate were sandwiched with a thin film of an aqueous NaCl solution (4.0 M) to reduce temporal fluctuation of SERRS intensity. This reduction may be due to the formation of $H_2TPP$−adatom−Cl anion complexes.[5,13] The appearance of SERRS-active Ag particles was found to be clumps of several Ag nanoparticles by SEM measurements, as reported by other groups (data not shown).[2,3,4,7,9,10,19]

The spectroscopic setup used in the current work is reported elsewhere.[16−19] Briefly, a SERRS-excitation light beam from an $Ar^+$ laser (457 nm) was focused on a sample glass surface with use of an objective lens (5×, N.A. 0.15). The incident angle of the light beam was 70° with respect to the sample plain. Excitation intensity was 40 mW/cm². SERRS and background-light emission from the identical Ag nanoaggregates were collected with an objective lens (60×, N.A. 0.15) and led to a polychromator (Pro-275, Acton, Tokyo), which was equipped with a thermoelectric cooling charge-coupled device (DV434-FI, Andor, Tokyo). Two different gratings (150 and 1200 grooves/mm) were used for detection of SERRS (spectral resolution: 3 cm⁻¹) and SERRS plus background-light emission (spectral resolution: 12 cm⁻¹), respectively. White light from a 50-W halogen lamp was introduced to the common focusing area by using a dark-field condenser to identify single Ag particles as isolated plasmon resonance Rayleigh scattering spots.

### Results

**Dark-Field and SERRS Optical Image of Ag Nanoaggregates.** Figure 1A shows Rayleigh scattering spots from Ag particles the color of which varied from one spot to another. Figure 1B shows inelastic scattering spots that correspond to SERRS-active Ag particles. Several literature reports and our own investigations identified SERRS-active Ag particles as nanoscale aggregates of Ag nanoparticles;[2,3,7,9,10,17,19] thus, we call SERRS-active Ag particles SERRS-active Ag nanoaggregates in the current work. However, this does not mean that all SERRS-active particles are large aggregates; indeed, isolated single Ag nanoparticles and dimers can also be SERRS active.[20−22] From the comparison between Figures 1A and 1B, we identify SERRS-active Ag nanoaggregates in Figure 1A. All SERRS-active Ag nanoaggregates in Figure 1B showed temporal intermittence known as "blinking", as will be discussed later with reference to Figure 3. The "blinking" of SERRS is attributed to either thermal translational and rotational motion of an adsorbed molecule on a SERRS-active site[1−4,6−9] or fluctuation of energy levels of a complex formed between a metal atom and an adsorbed molecule due to a change in the local work function at a SERRS-active site.[5] However, it may be considered that blinking of SERRS may not be always related to single-molecule detection.[30−32] The relatively high concentration of $H_2TPP$ used in the current work is also far from single-molecule detection condition if all of $H_2TPP$ molecules is adsorbed on Ag nanoaggregates. The left panel of Figure 1C shows a representative TEM image of Ag nanoaggregates. The right panel of Figure 1C shows an enlarged TEM image of an Ag nanoaggregate in which a junction of two Ag nanoparticles was clearly observed. Figure 1D shows a structure of a $H_2TPP$ molecule, which is an aromatic macrocycle with four pyrrole rings connected by unsaturated (methine) carbon atoms. The symbols of $\alpha$, $\alpha'$, $\beta$, and $\beta'$ in $H_2TPP$ molecule identify the positions of carbon atoms. Note that the symbol $C_\alpha$ is defined as a carbon atom which is bonded to a non-hydrogenated N atom in a pyrrole ring.

**Temporal Fluctuation of SERRS Spectra.** Figure 2A shows a resonance Raman spectrum of $H_2TPP$ powder on a glass surface. Figure 2B−D shows time-averaged (85 s) SERRS spectra from three independent Ag nanoaggregates that were adsorbed with $H_2TPP$ molecules. The positions of SERRS bands, except for the following key band, are the same as those of the resonance Raman bands in Figure 2A within an error of ±3 cm⁻¹. This error is within the resolution of the current spectroscopic system. Thus, SERRS-active $H_2TPP$ molecules were not decomposed or carbonized by high laser flounce. Figure 2B−D shows that a key Raman band was observed at 1357 cm⁻¹, which was not observed in the resonance Raman spectrum in Figure 2A. We have compared reference data of a resonance Raman spectrum of $H_2TPP$ with our SERS spectra,[33] and attributed this 1357 cm⁻¹ band to a $C_\alpha$−N stretching mode.
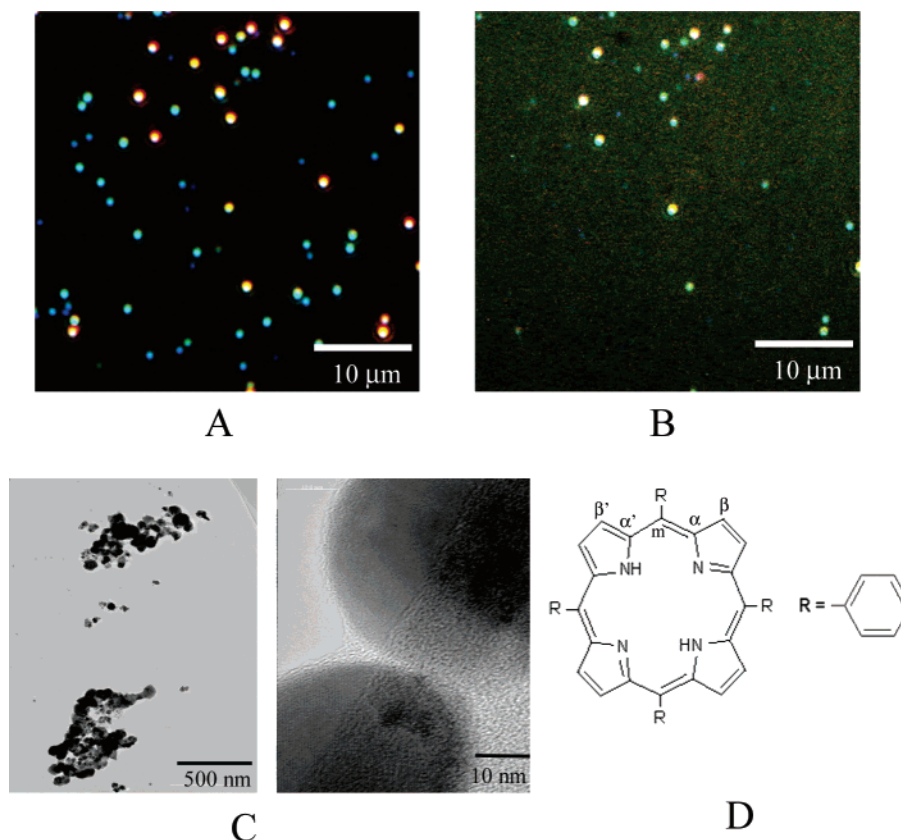
**Figure 1.** (A) Plasmon resonance Rayleigh scattering image of Ag nanoaggregates, (B) a corresponding SERRS image of Ag nanoaggregates, (C) a representative TEM image of Ag nanoaggregates, and (D) a molecular structure of metal-free $H_2TPP$.
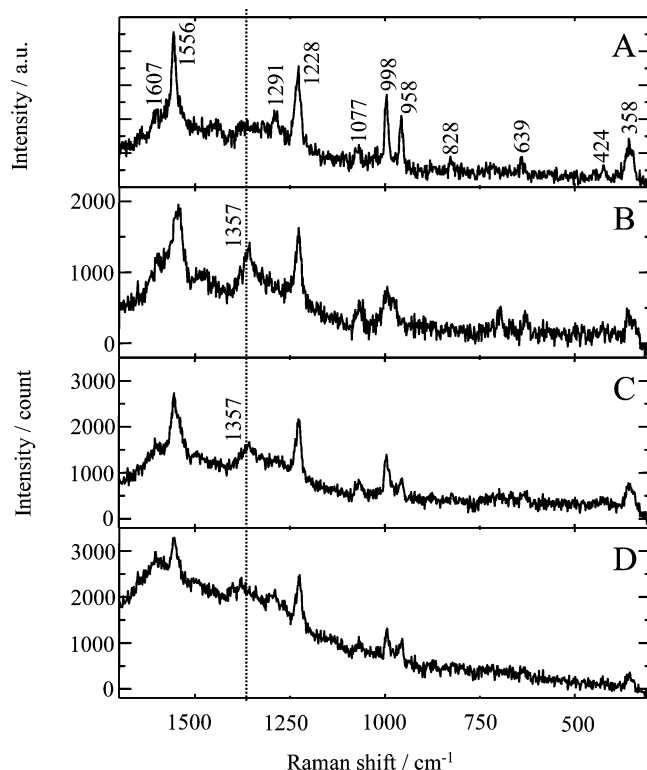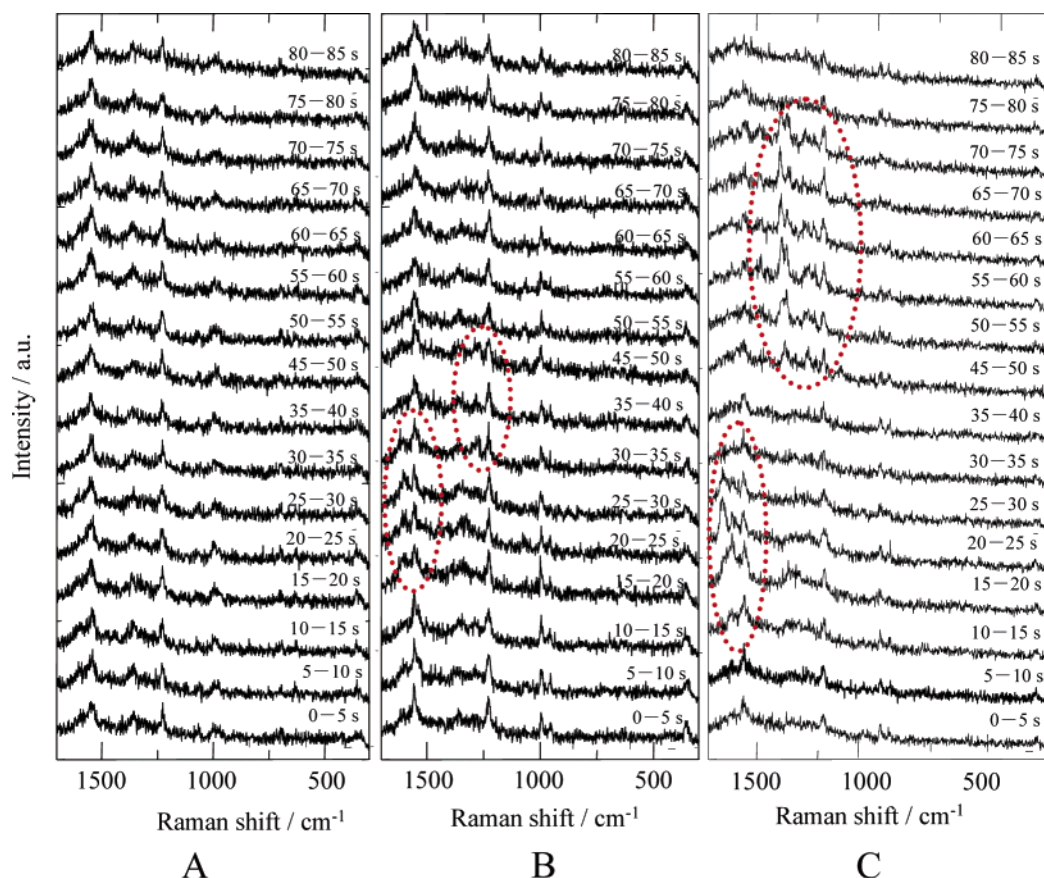


**Figure 2.** (A) Resonance Raman spectrum of $H_2TPP$ and (B–D) SERRS spectra of $H_2TPP$ molecules adsorbed on three different single Ag nanoaggregates.

It has been known that a $C_\alpha$–N stretching band appears at 1357 cm$^{-1}$ in a resonance Raman spectrum[33] and 1340 cm$^{-1}$ in a SERS spectrum.[25,26] In the current work, the presence of a high concentration of chloride ions is likely responsible for the

discrepancy observed in the wavenumber of the $C_\alpha$–N stretching mode. It has been widely known that nitrogen lone pair electrons have affinity to the Ag surface.[11] Thus, Ag–N bonding is likely to be present between $H_2TPP$ molecules and Ag surfaces; the chloride ions affected orbital overlap between nitrogen lone pair and Ag surfaces. Considering that Ag–N bonding is formed between $H_2TPP$ and Ag, the shifted $C_\alpha$–N band (from 1357 to 1340 cm$^{-1}$) may be due to enhanced stability of Ag–N bonding in the $H_2TPP$–adatom–chloride ion complexes. The stability of Ag–N bonding is likely reflected in the shifted $C_\alpha$–N stretching frequency. We missed observing a SERS band at 398 cm$^{-1}$, which is characteristic of an out-of-plain folding modes of pyrrole rings.[33] Probably, the presence of a high concentration of chloride ions on Ag surfaces prevented us from observing the band at 398 cm$^{-1}$. The out-of-plain folding modes of pyrrole rings include a plane perpendicular to a chloride ion layer on the Ag surface. Thus, the folding is likely to be suppressed by the chloride ions close to an Ag surface.

Figure 3A–C shows time-resolved SERRS spectra from three independent Ag nanoaggregates. Note that each SERRS spectrum in Figure 2B–D is reproduced by the summation of the time-resolved spectra in Figure 3, spectra A–C, respectively. The SERRS spectra in Figure 3A do not show a striking change with time. On the other hand, the SERRS spectra in Figure 3B,C show changes with time, as highlighted by red dotted circles. Figure 3B shows that Raman bands at 1602 and 1281 cm$^{-1}$ appeared and disappeared from 15–20 to 30–35 and 30–35 to 45–50 s, respectively. The Raman bands at 1602 and 1281 cm$^{-1}$ are attributed to a phenyl breathing mode and a $C_\alpha$–$C_\beta$ stretching mode, respectively.[25,26,33–35] Figure 3C shows that SERRS spectra prominently changed in frequency and intensity. The intensity of a phenyl breathing mode at 1602 cm$^{-1}$ increased

**Figure 3.** (A−C) Time-resolved SERRS spectra of H$_2$TPP molecules adsorbed on three different single Ag nanoaggregates corresponding to those in Figure 2B−D. Five seconds integration time per spectrum.

from 10−15 to 15−20 s, and then an unknown band at 1643 cm$^{-1}$ appeared from 20−25 to 25−30 s. This unknown band is likely $\nu_{10}$, which is one of the skeletal modes with the highest Raman shift.[33−35] Two bands at 1600 and 1643 cm$^{-1}$ simultaneously disappeared at 30−35 s. Then, the SERRS spectrum at 35−40 s returned to the initial one at 0−5 s. Next, Raman bands at 1268 and 1384 cm$^{-1}$ simultaneously appeared from 45 to 50 s. Furthermore, their sidebands at 1295 and 1398 cm$^{-1}$ also simultaneously appeared at 50−55 s.

**Temporal Fluctuation of Background-Light Emission.** We observed an intermittent property of background-light emission, which is also known as "blinking" in SERRS measurements.[1−9,19] To compare the blinking of SERRS and background-light emission, we simultaneously observed SERRS and background-light emission spectra by expanding a spectral window from 50 to 250 nm. Figure 4A shows fluorescence spectra of H$_2$-TPP. Fluorescence maxima at 650 and 720 nm are attributed to mirror-image transitions of Q-bands.[36] Figure 4B−F shows SERRS background-light emission spectra from five different Ag nanoaggregates. The highly structured bands observed around 460−500 nm are attributed to SERRS bands.[25,26] The background-light emission spectra can be divided into five bands, as in the vertical dotted lines at 690 ± 10, 620 ± 10, 590 ± 10, 560 ± 10, and 530 ± 10 nm. These emission maxima are different from the fluorescence maxima at 650 and 720 nm.

Figure 5A−C shows time-resolved background-light plus SERRS spectra of three different Ag nanoaggregates. Figure 5A shows that background-light emission and SERRS did not fluctuate largely with time. On the other hand, Figure 5B,C shows that background-light emission and SERRS fluctuated with time. Figure 5B shows that background-light emission was

a combination of two maxima at 590 and 610 nm indicated by two dotted lines from 0−5 to 15−20 s. The emission maximum at 590 nm increased, decreased, and disappeared from 0−5 to 30−35 s. The emission maximum at 610 nm increased and decreased from 0−5 to 30−35 s and kept its intensity from 35−40 to 80−85 s. During this temporal change, SERRS intensities and spectra also fluctuated. Figure 5C shows a background-light emission maximum at 560 nm shifted to 540 nm from 5−10 to 20−25 s, as indicated by arrow 1. Then, the emission maximum decreased and additionally shifted to 520 nm from 50−55 to 60−65 s, as indicated by arrow 2. During this time evolution of background-light emission, SERRS intensities and spectral shapes also fluctuated with time. Figure 5D,E,F shows trajectories of the intensity of the background-light emission maxima at 600, 600, and 550 nm (solid line with closed circles), respectively, and of the common SERRS maximum at 490 nm (dashed line with open circles) in Figure 5A,B,C, respectively.

## Discussion

**SERRS Blinking under the High-Molecular Concentration Condition.** From the comparison between parts A and B of Figure 1, we found that the color of Rayleigh scattering of SERRS-active Ag nanoaggregates is not blue, but always red or yellow. Indeed, the red or yellow color is an indication of aggregated Ag nanoparticles. The involvement of aggregated Ag nanoparticles as SERRS-active Ag particles is consistent with the previous work that revealed that an aggregate of Ag nanoparticles can be SERRS active.[2,3,7,9,10,17,19] From the previous work,[2,3,7,9,10,19] H$_2$TPP molecules located at the junction of nanoparticles are likely SERRS active. The "blinking" of
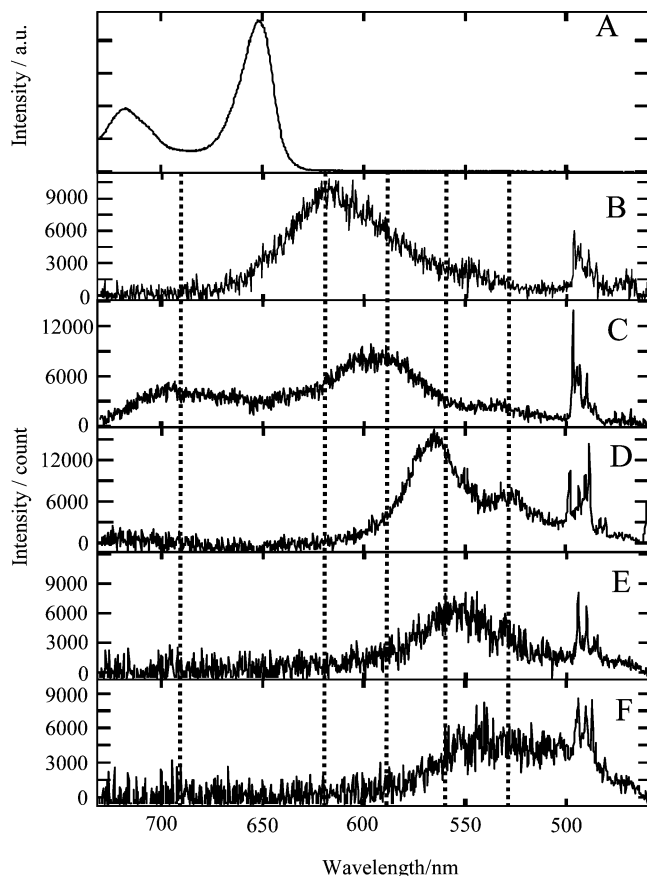
**Figure 4.** (A) Fluorescence spectrum of $H_2TPP$ and (B−F) variations in background-light emission spectra of $H_2TPP$ molecules adsorbed on single Ag nanoaggregates. The highly structured bands around 460−500 nm are SERRS bands.[20,21]

SERRS is attributed to either thermal diffusion of an adsorbed molecule on a SERRS-active site[1−4,6−9] or fluctuation of energy levels of a complex formed between a metal atom and an adsorbed molecule due to a changes in the local work function at a SERRS-active site.[5] Considering the above discussion of blinking,[1−9] the appearance of blinking in the current SERRS measurements suggested a possibility that the number of adsorbed molecules per one SERRS-active site in a nanoaggregate is closed to the single-molecule level. However, blinking may not always be related to single-molecule detection; there are reports relating blinking to some chemical reactions on Ag surfaces.[30−32] The relatively high concentration of $H_2TPP$ used in the current work is also far from the single-molecule detection condition if all of the $H_2TPP$ molecules are adsorbed on Ag nanoaggregates.

**Suppressed Fluctuation of SERRS and Background-Light Emission by Ag−N Bonding.** We found a key to understanding the interaction between Ag atoms and $H_2TPP$ molecules in SERRS spectra at 1357 $cm^{-1}$. This wavenumber is attributed to a $C_\alpha$−N stretching mode by comparing SERRS spectra in Figure 2B−D with a resonance Raman spectrum of $H_2TPP$ in Figure 2A. Kobayashi et al. reported that resonance Raman spectra of a complex of two Ag atoms and one $H_2TPP$ molecule show the strong band of a $C_\alpha$−N stretching mode,[25,26] whereas the resonance Raman spectrum of $H_2TPP$ does not show a $C_\alpha$−N stretching mode. Thus, formation of an Ag−N bond is evidenced by the appearance of a $C_\alpha$−N stretching mode in the SERRS spectra in Figure 2B−D. Furthermore, formation of Ag−N bonds between adsorbed molecules with non-hydrogenated N atoms and Ag surface atoms is favored by

reduction of the work function of Ag surfaces, as revealed by ultraviolet photoemission spectroscopy (UPS).[37] Thus, our identification of the Ag−N bonds between $H_2TPP$ molecules and Ag surfaces in SERRS spectra is consistent with the previous experimental observations.

Recently, Jarzecki and Spiro applied a method of density functional theory (DFT)/configuration interactions with single-excitation (CIS) to analyze resonance Raman spectra of metal-free porphines.[34] Changes in the current SERRS spectra are quite similar to a change in their calculated spectra, which is caused by electronic excitation splitting (Figure 3 in ref 28). The electronic excitation splitting is caused by two kinds of N atoms in a pyrrole ring, one is hydrogenated and the other is non-hydrogenated, as shown in Figure 1D. The two kinds of nitrogen atoms in a pyrrole ring split the excitation into two kinds of polarization.[34] In particular, a temporal change in the observed spectra in Figure 3B,C, which are highlighted by dotted circles, are in agreement with the transition from one polarized resonance Raman spectrum to the other polarized one of $H_2$-TPP.[34] Assuming that the current measurement is implemented at the single-molecule level per one SERRS-active site, the temporal change in SERRS bands in Figure 3B,C may provide evidence for rotation of a $H_2TPP$ molecule against a SERRS-excitation electromagnetic field localized on a SERRS-active site.

The SERRS spectrum in Figure 2B, which was averaged over stable time-resolved spectra in Figure 3A, clearly shows a $C_\alpha$−N stretching mode at 1357 $cm^{-1}$, whereas the SERRS spectra in Figure 2C,D, which were averaged over unstable time-resolved spectra in Figure 3, spectra B and C, respectively, do not clearly show the $C_\alpha$−N stretching mode. Thus, the $C_\alpha$−N stretching mode in Figure 2B supports the idea that a $H_2TPP$ molecule forms a stable Ag−N bond with a surface Ag atom. On the other hand, an unclear $C_\alpha$−N stretching mode in Figure 2C,D supports that a $H_2TPP$ molecule forms an unstable Ag−N bond with a surface Ag atom. From the two types of appearance of a $C_\alpha$−N stretching mode, we consider that the origin of temporal fluctuation of SERRS spectra is due to fluctuation of an Ag−N bond between a surface Ag atom and a $H_2TPP$ molecule. We consider a possible origin of stable and unstable Ag−N bonds is temporal fluctuation of the local work function of an Ag surface, which changes the barrier height of electron tunneling from that of a chemisorbed molecule to that of an Ag surface or that of an Ag surface to that of a molecule.[5]

We identified in the previous paragraph a $C_\alpha$−N stretching mode that is an indication of an Ag−N bond between a $H_2TPP$ molecule and a surface Ag atom when SERRS spectra are temporally stable. Figure 5D shows that background-light emission was well synchronized with SERRS when the emission and SERRS were temporally stable. Figure 5E,F shows that background-light emission is out of synchronization with SERRS when both the emission and SERRS are temporally unstable. The out of synchronization, together with the synchronization, suggests that the Ag−N bond determines not only the temporal fluctuation of SERRS but also that of the background-light emission.

**Proposed Mechanism of SERRS and Background-Light Emission in the $H_2TPP$/Ag Nanoaggregate System.** Figure 4A−F shows blue shifts of background-light emission maxima from fluorescence maxima. These blue shifts suggested that background-light emission is not fluorescence of free $H_2TPP$ molecules. Background-light emission of SERRS has been considered to be luminescence or electronic Raman scattering from complexes of chemisorbed molecules and surface metal
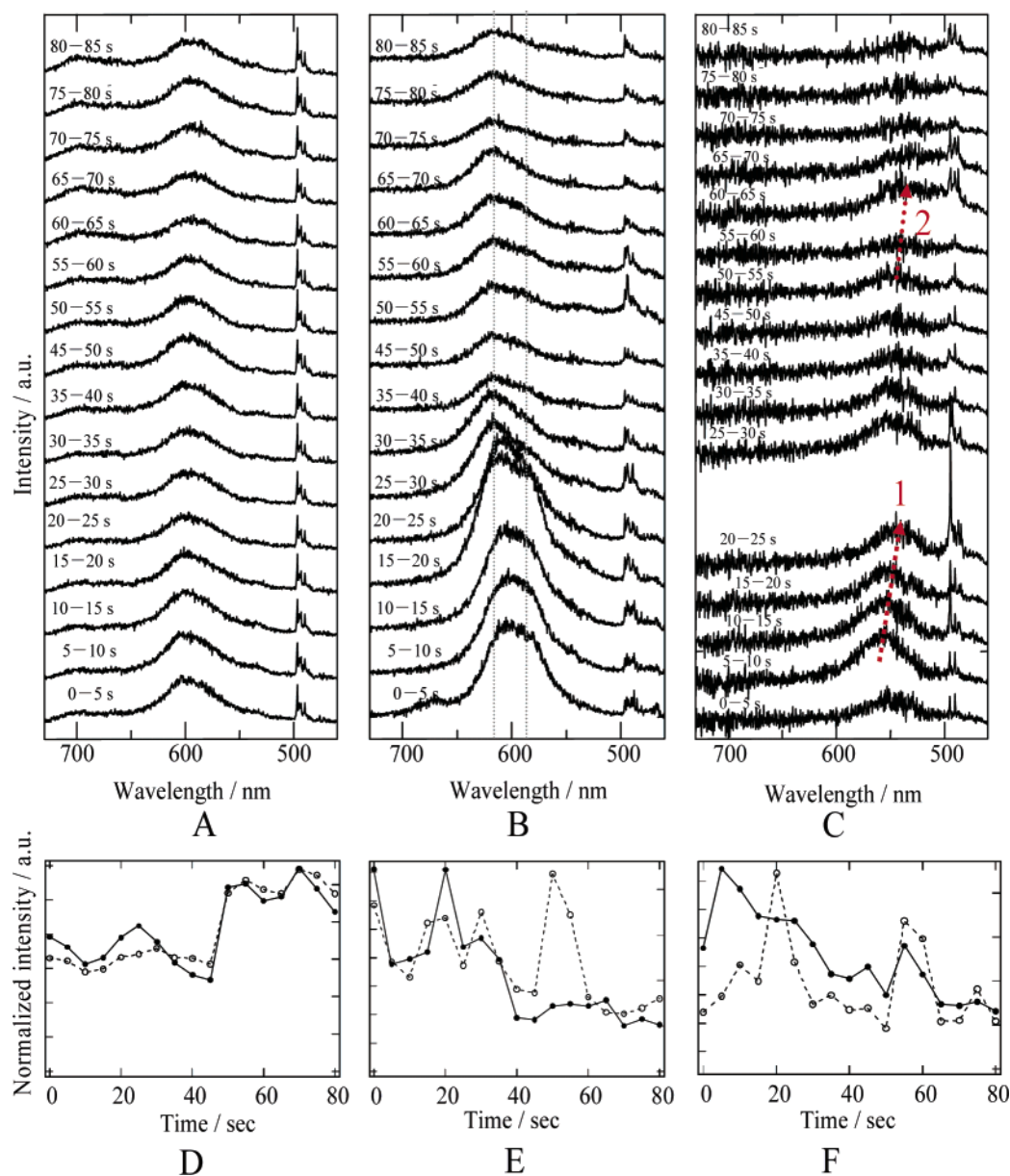
**Figure 5.** (A−C) Time-resolved background-light emission spectra of $H_2TPP$ molecules (5 s integration time) adsorbed on single Ag nanoparticle aggregates and (D−F) trajectories of the intensity of the background-light emission maxima at 600, 600, and 550 nm (solid line with closed circles), respectively, and of the common SERRS maximum at 490 nm (dashed line with open circles) in parts A, B, and C, respectively. Intensities of the trajectories are normalized to their maximum intensity.

atoms.[4,7,11,12,19,23] We have observed the lack of excitation-wavelength dependence of background-light emission maxima for the $H_2TPP$/Ag nanoaggregate system (data not shown). The lack of excitation-wavelength dependence supports the idea that background-light emission is not Raman scattering but luminescence. Furthermore, we have identified in the previous section that SERRS-active $H_2TPP$ molecules form Ag−N bonds with surface Ag atoms. From the lack of excitation-wavelength dependence and formation of Ag−N bonds, we attributed the background-light emission to luminescence of $H_2TPP$−Ag complexes. From the point of the origin of luminescence, we assumed that the observed five background-light emission maxima in Figure 4B−F are luminescence from several conformations of $H_2TPP$−Ag complexes, because surface conformations of chemisorbed molecules on metal surfaces strongly change the electronic orbital of the molecules.[5,11,15] However, there is still difficulty in identifying the origin of the luminescence because the out of synchronization between SERRS and background-light emission suggests a possibility

that SERRS is occasionally detected without background-light emission, and vice versa. We considered that SERRS without background-light emission is Raman signals of $H_2TPP$ molecules, not forming complexes with Ag atoms, enhanced by the EM field at SERRS-active sites, and that background-light emission without SERRS is luminescence from Ag-atom clusters,[38,39] which was enhanced by a strong EM field at SERRS-active sites.

We have difficulty in identifying electronic structures of $H_2$-TPP−Ag complexes because no general rules are available to identify the structures. Furthermore, formation of orbital mixing between molecules and metal surfaces depends strongly on the combination of molecules and metals.[11,15] Ishii et al. investigated electronic structures of $H_2TPP$ molecules on several kinds of metal surfaces by UPS.[27−29] They showed that the decrease in the vacuum level energy of $H_2TPP$/Mg, $H_2TPP$/Ag, and $H_2$-TPP/Au systems is 0.3, 0.6, and 1.0 eV, respectively, and noted that these variations in the reduction of vacuum level indicate the existence of an electronic state at an interface between $H_2$-

TPP molecules and a metal surface.[27−29] They also commented that decreases in a vacuum level energy indicate charge transfer (CT) from $H_2TPP$ molecules to metal surfaces through the interface electronic state.[28] Lombaridi et al. developed SERRS mechanisms including the CT from adsorbed molecules to metal surfaces (Figure 1C in ref 14). According to the CT-SERRS mechanisms[14] and a comprehensive dipole−dipole interaction theory,[24] one possible quantum mechanical picture of SERRS and background-light emission of the $H_2TPP$/Ag nanoaggregate system is summarized in the following manner. The incident light that is enhanced by a plasmon dipole excites an electron in one HOMO state of a molecule to an interface electronic state between a molecule and a Ag nanoaggregate, and then the excited electron is scattered back to the initial HOMO state. The coupling between the transition-up dipole, which is induced by excitation from a HOMO state to an interface state, and a plasmon dipole enhances the scattering process. This enhanced scattering is the origin of SERRS.[24] On the other hand, a portion of the population of an excited electron in the interface electronic state can radiatively decay to the initial HOMO state. The coupling between the transition-down dipole, which is induced by radiative decay from the excited interface electronic state to the initial HOMO state and plasmon dipole enhances the radiative decay process. This enhanced radiative process is an origin of background-light emission.

## Conclusion

We have investigated both temporal changes of SERRS and background-light emission spectra of $H_2TPP$ adsorbed on Ag nanoaggregates. When SERRS spectra were temporally stable, a $C_\alpha$−N stretching mode was clearly observed in SERRS spectra. On the other hand, when SERRS spectra were temporally unstable, this mode was not clearly observed. Furthermore, when SERRS spectra were temporally stable, the intensity of background-light emission was synchronized with the intensity of SERRS. Furthermore, when SERRS spectra were temporally unstable, the intensity of background-light emission was temporally unstable and was not synchronized with the intensity of SERRS. A $C_\alpha$−N stretching mode is enhanced when $H_2$-TPP molecules form Ag−N bonds with surface Ag atoms.[25,26] Thus, we attributed the spectral fluctuation of SERRS and background-light emission to fluctuation of Ag−N bonds, the control of which plays an important role in suppression of spectral fluctuation. Furthermore, we attributed background-light emission to luminescence of complexes between $H_2TPP$ molecules and surface Ag atoms considering possible Ag−N bonds, synchronized SERRS intensity with background-light emission intensity, blue shifted background-light emission maxima from normal $H_2TPP$ fluorescence maxima, and the literature reports on electronic structure of $H_2TPP$ molecules on Ag surfaces.[27−29]

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