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Journal of Photochemistry and Photobiology A: Chemistry 194 (2008) 356–361

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Short communication

Resonance Raman process and photo-induced phase transition via 632.8 nm irradiation for diacetylene monocarboxylic acid derivative self-assembled layers on Ag surfaces

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Received 3 May 2007; received in revised form 31 July 2007; accepted 21 August 2007
Available online 24 August 2007

Abstract

Photo-induced interfacial behaviors of a diacetylene monocarboxylic acid derivative 10,12-pentacosadiynoic acid (PCDA) on Ag substrates have been examined by means of surface enhanced Raman scattering (SERS) as a function of irradiation time upon excitation at 632.8 nm close to the blue phase's maximum absorption at ∼625 nm. Photoreactions on a SERS-active spot appeared to differ from those on a SERS-inactive substrate. On a SERS-inactive Ag plate, laser excitation at 632.8 nm led to the exhibition of longer conjugation length blue phase PCDA than red phase via a resonance Raman process. On a roughened SERS active Ag plate, as the irradiation time elapsed, PCDA appeared to exhibit a blue-to-red phase transition even under excitation at 632.8 nm and the subsequent photo-degradation. Raman mapping of the C=C stretching band intensity change at $\sim 1450\,\text{cm}^{-1}$ for the blue phase, with respect to that at $\sim 1500\,\text{cm}^{-1}$ for the red phase, can be utilized as a new method of photo-induced micro-patterning on SERS active surfaces.

Keywords: 10,12-Pentacosadiynoic acid (PCDA); Ag; Photoreaction; SERS; Micro-Raman mapping

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1. Introduction

Stimuli-responsive materials are of widespread fundamental interest due to their potential applications such as rapid detection of dangerous biological agents [1] and highly dense information storage [2]. Since works on the solid-state polymerization of diacetylene [3], polydiacetylene's chemistry and physics have become an integral part of modern polymer science [4]. Researchers have investigated whether heat, pH, UV or gamma-ray irradiation can induce polymerization of diacetylene derivatives [5–9]. The polymerization of diacetylene has been known to result in the formation of a deep blue color ($\lambda_{\max} \sim 625$ nm, blue phase) that changes to an intense purple-red color ($\lambda_{\max} \sim 540$ nm, red phase). Although the mechanism of this blue-red phase transition is not fully established, it has been proposed that the key to the transition is the interplay between the conformation of the pendant side groups and the backbone [5]. This chromism is known to be associated with variations in the effective conjugation length of polydiacetylene backbone structure. This chromogenic transition has been harnessed for the purpose of chemical and biological sensors [10,11].

The color change can be interpreted as a structural disorder of the side chains group linked to the polyacetylene backbone and the electronic states [6]. The transition of the blue phase with a regular *trans*-zigzag structure of the *trans*-alkyl side chains proceeds to the red phase of an irregular structure containing gauche conformations. This conversion accompanies shifts in the C≡C and C=C stretching resonance Raman scattering bands from ∼2090 and $\sim 1450\,\text{cm}^{-1}$ for the blue phase to ∼2110 and $\sim 1500\,\text{cm}^{-1}$ for the red phase, respectively [12]. Polydiacetylene's blue-to-red phase transitions were found to occur differently depending on the excitation wavelength. The

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doi:10.1016/j.jphotochem.2007.08.017

transition temperature at 632.8 nm was observed to be higher than that at 568.2 nm [6].

Ultrathin films have received much attention due to their potential applications in electronic devices, colorimetric sensors, and surface-sensitive probes [13]. Vibrational spectroscopy can provide the energetics or phase transition of adsorbates on metal surfaces [14–16]. Surface-enhanced Raman scattering (SERS) as a surface vibration spectroscopic method has been utilized as a convenient technique to investigate self-assembled monolayers (SAMs) on metal surfaces [17–19].

It has been predicted that photochemistry should be enhanced on rough surfaces [20]. In the recent Raman microscopic work [21], the 532-nm-induced polymerization and bleaching processes of PCDA appeared to be enhanced by SERS-active substrates. Several resonance Raman works [6,12,21] on the phase transition of diacetylene derivative films have been reported. Carboxylic acids can produce self-assembled monolayers on metal surfaces such as Ag and Cu [22]. Although 632.8 nm irradiation is a good excitation source for obtaining various SAMs on several metal surfaces [23], a combined study with SERS active spots and laser excitation at 632.8 nm resonating with the blue phase of 10,12-pentacosadiynoic acid (PCDA), however, has not yet been examined, to the best of the authors' knowledge.

In this work, to better understand diacetylene materials' interfacial structure and photoreaction, we performed a SERS study of PCDA self-assembled layers adsorbed on rough Ag plate surfaces and SERS inactive Ag plates under irradiation at 632.8 nm close to the blue phase's maximum absorption. Our work may be utilized to develop a facile photo-induced method of micro-patterning polydiacetylene self-assembled thin film on SERS-active metal surfaces.

2. Experimental

2.1. Sample preparations

PCDA (>98%) was purchased from Fluca. The Ag SERS substrate [14,24] was prepared by eroding the Ag plate using a HNO_3 solution or an oxidation–reduction cycle using a CH Instruments 700A potentiostat. Before immersing the Ag substrates in the ethanolic solution of PCDA, the substrates were rinsed with excess ethanol and dried by an N_2 gas stream. After the self-assembly of PCDA, the substrates coated with the PCDA were rinsed with excess ethanol and dried with an N_2 gas stream again. We also used a Langmuir trough (Nima Technology Model 312D) for fabricating the LB film, and could not find a significant difference from the film prepared by self-assembly. In order to confirm that SAMs of PCDA are fabricated on Ag surfaces, we performed an attenuated-total-reflection spectroscopy study on the surfaces of Ag micro-particulate powders using a FT-IR spectrometer (Thermo Nicolet 6700) with the accessory (PIKE Technology Miracle HATR). Although not shown here, the C=O band observed in the near infrared spectrum of PCDA completely disappeared after the self-assembly on Ag surfaces. This result indicates PCDA should form the SAMs on Ag via a carboxylate form.

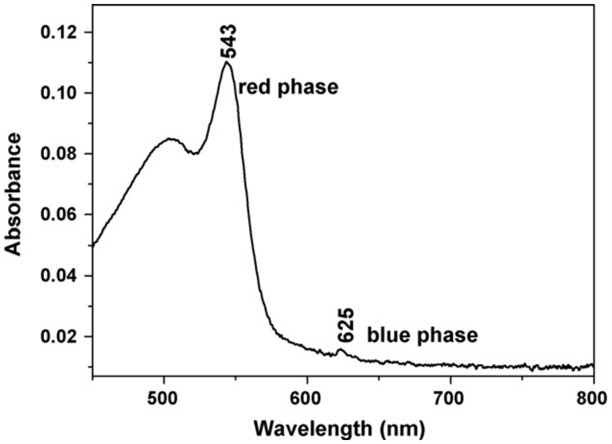

Fig. 1. UV–vis absorbance spectrum of (10 mM) PCDA in ethanol.

2.2. UV–vis and Raman measurements

UV–vis absorption spectra of PCDA in ethanol were obtained with a Shimadzu UV-3101PC spectrophotometer. The absorption peaks corresponding to the red and blue phase were observed at ~543 and ~625 nm, respectively, as shown in Fig. 1. Raman spectra were obtained using a Renishaw Raman confocal system model 1000 spectrometer equipped with an integral microscope (Leica DM LM). The irradiated sample area was estimated by ca. 2 μm × 2 μm. The 632.8 nm irradiation from a 20 mW air-cooled HeNe laser (Melles Griot Model 25 LHP 928) with the plasma line rejection filter were used as the excitation sources for the ordinary Raman and SERS experiments. The holographic grating (1800 grooves/mm), and the slit allowed the spectral resolution to be 1 cm^{-1}. The Raman band of a silicon wafer at 520 cm^{-1} was used to calibrate the spectrometer, and the accuracy of the spectral measurement was estimated to be 1 cm^{-1}. It took approximately 90 s for each Raman scan in a full range between 150 and 2500 cm^{-1}. A custom-built mapping stage was used for *xy* translation with a sub-micrometer mechanical resolution. To obtain a mapping image, it took approximately 1 s to take a single Raman spectrum in a narrow region between 1200 and 1700 cm^{-1} to take the C=C bands at ~1450 and ~1500 cm^{-1} for the blue and red phase, respectively. The sample was moved by 1 μm after finishing each scan. To raise a photo-induced change, the sample was irradiated for ca. 50 min. We have not introduced any UV light to raise a polymerization reaction for the present experiment.

3. Results and discussion

3.1. Resonance Raman spectra on SERS inactive Ag plates

Upon irradiation at 632.8 nm at a SERS-inactive spot, the vibrational bands of PCDA began to increase in intensity as shown in Fig. 2. The bands associated with the CH_2 rocking and wagging (or twisting) vibrational modes can be found at 695 and 1040–1380 cm^{-1}, respectively. The prominent vibrational bands at 1458 and 2106 cm^{-1} could be assigned to the ν(C=C) and ν(C≡C) bands, respectively. The Raman frequencies are in

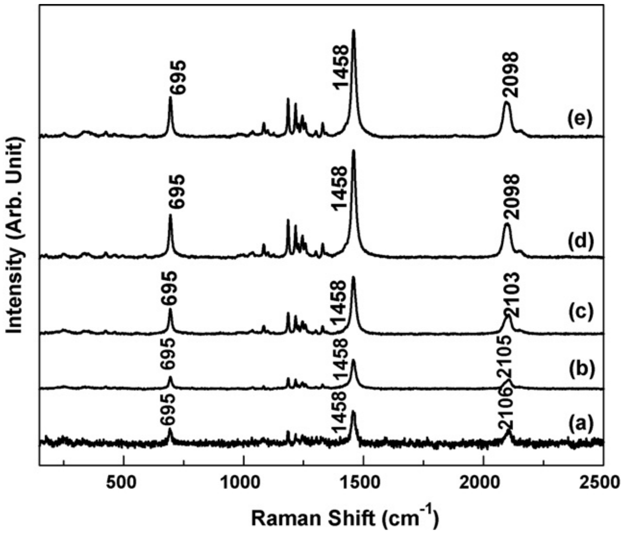

Fig. 2. Resonance Raman spectra on a Ag plate after irradiation of 632.8 nm for (a) 30 s, (b) 27 min, (c) 57 min, (d) 125 min and (e) 180 min. The spectral measurement time for each scan is identical.

good agreement with measurements for blue phase diacetylene derivative crystalline solids [12]. Fig. 2 shows a representative series of resonance Raman spectra as a function of irradiation time acquired for 632.8 nm. This result should be due a resonance Raman effect under the irradiation at 632.8 nm for the blue phase whose absorption maximum locates at ca. 625 nm. It has to be mentioned that the overall spectral intensities increase considerably as irradiation time. The ν(C≡C) bands were found red-shifted from 2106 to 2098 cm^{-1}. All the other bands did not exhibit a great frequency shift. In the ordinary Raman (OR) spectrum of PCDA as shown in Fig. 3a, the ν(C≡C) band was observed at 2096 cm^{-1}. In order to figure out the cause of the increase in the Raman intensity, we checked a possibility of the heating effect by increasing the sample temperature on SERS-active Ag plate surfaces. The Raman intensities for the blue phase PCDA appeared to increase approximately by a factor of 7 in slightly increasing temperature from 28 to 42 °C. These results indicate that the increase in Raman intensity shown in Fig. 2 could be due to a photo-irradiated heating as well as a resonance Raman process. The intensities of the blue phase became considerably decreased however and converted to the red phase from 50 to 87 °C. It seems that the changes in Raman intensity depending on the irradiation time as shown in Fig. 3 were not greatly enhanced by temperature. For the SERS-inactive spot, by changing temperature, we could not obtain the consistent SERS spectra as shown in Fig. 2. The peaks positions indicate a systematic formation of the blue phase PCDA as previously reported [12]. To compare the structural change on the surface, we performed a SERS study on a roughened Ag plate.

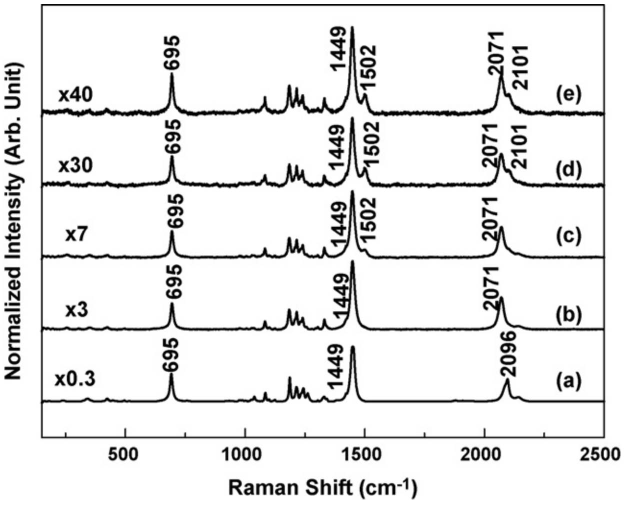

Fig. 3. (a) OR spectrum of PCDA and SERS spectra on roughened Ag plate taken at (b) 2 min, (c) 14 min, (d) 43 min and (e) 102 min. The spectral measurement time for each scan is identical. The spectral intensities are normalized for a better comparison. The magnification (or reduction) factor is marked on the left-hand side of each Raman spectrum. For example, the intensity of (e) is magnified by a factor of 40 indicating the signal decrease.

3.2. SERS spectra on Ag plates

The ordinary Raman (OR) spectrum of PCDA is shown in Fig. 3a. Their peak positions with appropriate vibration assignments [25,26] are listed in Table 1. As shown in Fig. 3, it was rather straightforward to correlate the OR bands with the Ag SERS bands. The CH_2 rocking vibrational mode can be found at 695 cm^{-1} in Ag SERS spectra. The ν(C=C) and ν(C≡C) bands were found at 1449 and 2071 cm^{-1}, respectively.

It is noteworthy that the ν(C≡C) band were found to be quite redshifted by 25 cm^{-1} from 2096 cm^{-1} in the OR spectrum to 2071 cm^{-1} in the SERS spectrum. This result indicated a substantial interaction of PCDA on Ag. The decrease in spectral frequency upon adsorption on Ag indicated that the broad features at ∼2071 cm^{-1} should be due to the relative unstable one in comparison with the neat state at ∼2096 cm^{-1}. Intriguingly, the C=C double bond did not show such a redshift as the C≡C triple bond upon adsorption on a Ag surface. The redshifts in the SERS spectra of the aromatic adsorbates are assumed to be due to a flat stance of the benzene ring system with respect to the metal surfaces [27]. Analogously, the triple bond of PCDA may lie parallel with respect to the surface, whereas the double bond has a rather perpendicular orientation as later depicted in

Table 1
Spectral data and vibrational assignment of PCDA

OR	Ag plate SERS	Assignment[a]
CH_2		
695	695	CH_2 rock
1040–1380	1080–1340	CH_2 wag + twist
C=C		
1449	1449	ν(C=C) blue
	1502[b]	ν(C=C) red
C≡C		
2096	2071	ν(C≡C) blue
	2101[b]	ν(C≡C) red

Unit in cm^{-1}.

[a] Based on Refs. [25,26].

[b] Measurements are taken after irradiation for ca. 50 min.

Fig. 5a. The different orientations of the triple and double bonds with respect to the surfaces are presumably assumed to cause the dissimilar behaviors in spectral shifts after the adsorption on Ag.

As a function of irradiation time, it is noteworthy that a new feature for the ν(C=C) band began to appear at ~1502 cm^{-1} corresponding to the red phase as well as the band at ~1449 cm^{-1} corresponding to the blue phase as shown in Fig. 3c–e. It is not absolutely certain why the frequency positions of ν(C=C) bands are found to be ~17 cm^{-1} lower than those from the previous experiment conducted at 532 nm [21]. This difference may be due to the different excitation wavelength at 632.8 nm. From the resonance Raman works of polydiacetylene monolayers, the frequency positions of the ν(C=C) bands were found to be different depending on the excitation wavelengths [6,12]. We have also to mention that the UV-irradiation was not employed for the present study for a photoconversion and that the different samples were used as SERS active and inactive substrates.

Along with changes, the ν(C≡C) band was found at 2101 cm^{-1} for the red phase as well as that at 2071 cm^{-1} for the blue phase. The overall SERS spectral intensities appeared to decrease as a function of irradiation time. As marked in the magnification factor of each Raman spectrum in Fig. 3, the intensities decreased as the irradiation time continued. This result indicated that PCDA assembled on SERS-active Ag plate surfaces should undergo a photo-degradation. A photoconversion process as in the previous report [21] is assumed to occur for the present study. Considering that the overall spectral intensities diminished as the elapsed time increased, a substantial part of the PCDA adsorbates appeared to decompose on the SERS-active Ag surfaces. From the electromagnetic theory of SERS, a surface roughness should be important to obtain the large Raman signal and minimize the photo-degradation [28]. It has to be mentioned that not only the photo-degradation effect but also the electromagnetic field effect from the SERS substrate may affect the overall spectral pattern. We plan to study the photo-conversion process on various SERS active substrates at different laser powers and wavelengths to elucidate the surface reaction of PCDA.

The interaction between the acetylene moiety and roughened metal surfaces may strongly perturb the PCDA phase. As exhibited in Figs. 2 and 3, a detailed information on the phase transitions of PCDA could be obtained however as in the case of the Raman spectrum of the neat sample. In our substrate-dependent spectra, it has to be mentioned that the adsorbate state of PCDA may be strongly influenced by surface conditions. As discussed in the recent report [21], the different spectral behaviors in Figs. 2 and 3 should be related to the SERS activity of Ag substrates. Considering that our SERS active Ag plates have quite a rough surface in comparison with the size of PCDA, it is admitted that surface roughness, morphology, and number of adsorbed molecules should also affect the results. Inferring from that the SERS spectra of PCDA on the surfaces of Ag micro-particulate powders gave a similar result with those on a roughened Ag plate surface, it is assumed that the SERS activity of the substrates should affect the photoreaction process.

As shown in the UV–vis absorbance spectrum of Fig. 1, the absorbance peak of the red phase at ~543 nm appeared to be much stronger than that of the blue phase at 625 nm. This may explain why we could observe the Raman peaks of the red phase located far off the resonance Raman region under our experimental condition. It is also possible that a wide range of chromatic phases such as the purple phase can exist and affect the Raman spectra during a photo-converted process under our experimental conditions. To utilize this photo-induced change, we obtained a Raman image of the blue-to-red transition using the two ν(C=C) stretching bands at ~1450 and ~1500 cm^{-1}. The mapping image can be obtained by determining the relative intensities of the two vibrational bands.

3.3. Mapping with the ν(C=C) stretching bands

To raise a photo-induced change, the sample was irradiated at 632.8 nm for ca. 50 min. The ν(C=C) stretching peaks on Ag showed multiple structures as the irradiation time elapsed as discussed in Fig. 3. Considering that the irradiated area in our confocal Raman spectrometer is estimated to be ~2 μm × ~2 μm, our results indicates that we can develop a photolithographic method using 632.8 nm irradiation for the PCDA film self-assembled on SERS active plates. As exhibited in Fig. 4, the mapping image can be obtained with a minute

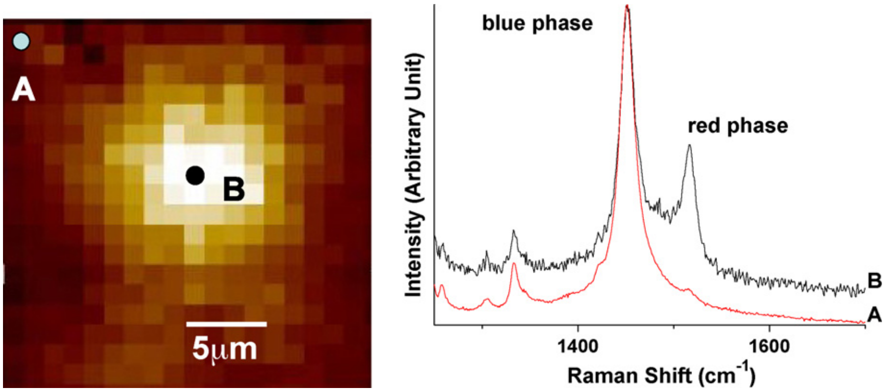

Fig. 4. Micro-Raman mapping in intensity for the blue phase with respect to the red phase for the SERS spectra on Ag. The whole mapping area is 20 μm × 20 μm. The two ν(C=C) bands at ~1450 and ~1500 cm^{-1} are compared to take the intensity ratio. The "A" and "B" spot correspond to the region that was irradiated by the 632.8 nm laser for ~45 s and ~50 min, respectively. The actual SERS spectra of "A" and "B" are illustrated in the right figure.

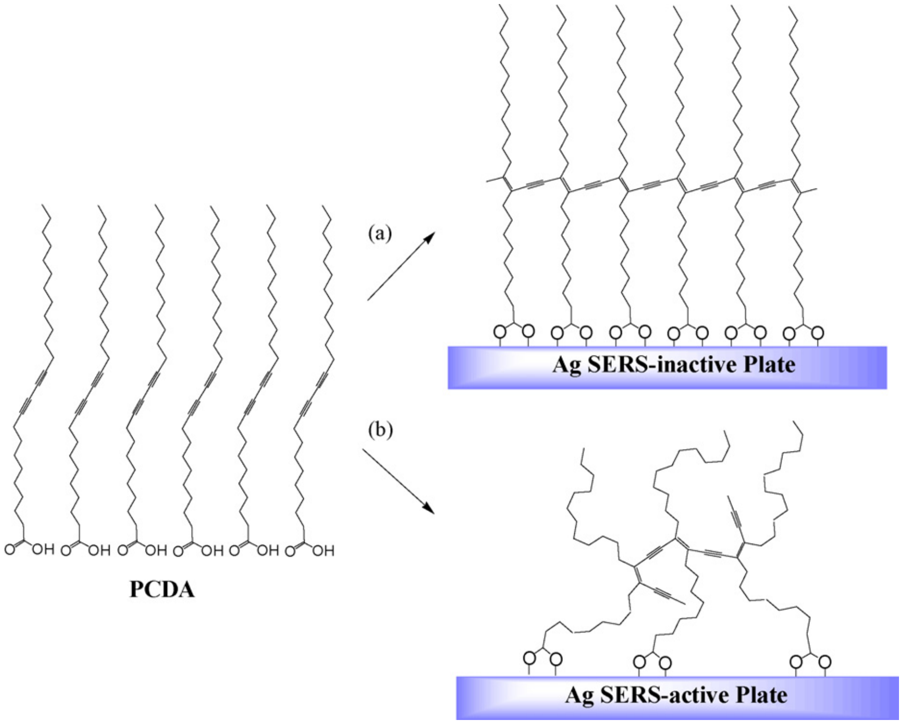

Fig. 5. Schematic diagram of the photoreaction process for PCDA layer via 632.8 nm irradiation on (a) SERS-inactive and (b) SERS-active Ag plates.

movement of the sample stage at a micrometer scale. The two ν(C=C) bands at ∼1450 and ∼1500 cm^{-1} are compared to take the intensity ratio. The "A" and "B" spot correspond to the region that was irradiated by the 632.8 nm laser for ∼45 s and ∼50 min, respectively. The bright "B" spot indicates the photo-converted area. Considering that the focused area via the He–Ne laser beam, we can produce a micro-patterned image via irradiation at 632.8 nm. Fig. 5 shows our schematic diagram of the photochemistry of PCDA self-assembled layers via 632.8 nm irradiation on SERS-inactive and SERS-active Ag plates. The model drawn in Fig. 5 is mainly based on the previous report [21]. The orientation of PCDA is inferred from our recent SERS studies [14,22–24,27]. We are currently investigating the kinetic behaviors for the PCDA SAMs on Ag to reduce the exposure time and obtain good quality of photo-images in an efficient way. Also, the presumably present intermediate phase may have different photobleaching rate than the blue-phase and affect our Raman spectra. We are planning to study such photoconversion process on surfaces by varying temperatures [21].

4. Conclusion

The resonance Raman process and PCDA's blue-to-red phase transition on Ag metal surfaces have been studied by means of surface-enhanced Raman spectroscopy. On SERS-inactive sites, laser excitation at 632.8 nm is utilized to monitor the longer conjugation length blue-phase PCDA backbone structure than the red phase. By increasing the irradiation-time on the SERS active sites, the C=C and C≡C stretching band intensities at ∼1450 and ∼2070 cm^{-1} for the blue phase changed to those at ∼1500 and ∼2100 cm^{-1} for the red phase, differently from the SERS-inactive plate. Subsequently a photo-degradation process occurred as the irradiation time elapsed. Our results indicate that the resonant Raman and photo-conversion processes can occur for PCDA film assembled on Ag metal plates depending on the substrate's condition.

Acknowledgements

This work was supported by Korea Research Foundation Grant (KRF-2006-015-C00196), the Korea Science and Engineering Foundation (KOSEF R01-2006-000-10017-0), the Korea Research Foundation (grant number R-14-2002-004-01000), and the Seoul R&BD Program. This work was supported by the Soongsil University Research Fund. S-W.J. thanks Mr. Bum Keun Yoo for helping experiments and Prof. Dong June Ahn for valuable discussion.

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