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Aggregation States of Organic Dye Molecules in Organic – Inorganic Hybrid Films Studied by Near-Field and Far-Field Fluorescence Spectroscopy

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Abstract. Near-field fluorescence spectroscopy in conjunction with far-field fluorescence and Raman spectroscopy has been applied to investigate the aggregation states of cyanine dye of 2-[5-(1,3-Dihydro-3,3-dimethyl-1-octadecyl-2H-indol-2-ylidene)-1,3-pentadienyl]-3,3-dimethyl-1-octadecyl-3H-indolium perchlorate (NK3175) molecules in the depth direction, from the nanometer-scale top surface to the bulk, in the hybrid films consisted of NK3175 and a clay compound (SWN). The far-field Raman spectra reveal that these hybrid films contained both NK3175 molecules which did not take part in the adsorption and those adsorbed on SWN. The near-field photoluminescence (PL) spectra in the outermost surface within ca. 30 nm exhibit a significant blue shift for the hybrid films as compared to their respective PL spectra in the bulk, implying that the top surface of these hybrid films becomes more polar and/or rigid in terms of the microenvironment around NK3175 molecules compared to the bulk of them, in contrast to the case for the other hybrid film which was prepared by the alternative method. These results provide new information on the aggregation states of organic dye molecules not only in the bulk but in the nanometer-scale top surface of organic-inorganic hybrid systems.

1. Introduction

Photoinduced spectral change such as optical reflectance, refractivity, and fluorescence of photo-functional organic dyes has been utilized for various optical devices, for example, memories and switching devices. In order to find out the method for the non-destructive readout which is one of the most pressing problems for photochromic memories [1], we proposed to monitor the absorption in the UV-visible region for the cooperative responsive system of a photochromic dye and a cyanine dye [2]. In this system, the photoinduced spectral change ascribed to a cyanine dye (NK3175) was generated by the hybridization of NK3175, a photochromic dye and an inorganic layered material of cation-exchangeable clay, smectite (SWN), with a simple preparation method [2]. Furthermore, we have found that the spectral change due to NK3175 was induced upon the irradiation of UV light without the help of photochromism, for the first time, by the hybridization of NK3175 and SWN [3]. Inorganic layered materials such as clay minerals are extensively utilized as host materials for functional organic-inorganic hybrid systems due to their characteristic properties of intercalation and adsorption of organic guest species such as organic dyes [4-9]. It has been reported that intercalation and adsorption of organic dyes promote aggregation and alignment of them in hybrid systems consisted of organic dyes and inorganic layered materials [4-5, 10-16]. The aggregation states of cyanine dyes



which are the best known self-aggregation dyes have been studied widely for the organic-inorganic hybrid systems [17]. In the above film hybridized with NK3175 and SWN the aggregation states of NK3175 molecules and the interaction between NK3175 and SWN might affect the microstructure and photoinduced spectral behavior. In this point of view it is of interest to investigate the aggregation states of NK3175 molecules in the above film.

It is well-known that the spectral properties of cyanine dyes are influenced by their aggregation [18]. Thus far, the structure of molecular assemblies and the aggregation states of cyanine dyes organized on silver halides [19-20] and clays [10, 21], etc. has been studied extensively by using spectroscopic methods such as electronic absorption and fluorescence spectroscopy. Near-field scanning optical spectroscopy (NSOM), which has been developed recently, is high resolution probe techniques on nanometer length scale beyond the diffraction limit [22]. Near-field fluorescence spectroscopy, one of these techniques, has been used to study nanostructured thin-film materials, including aggregated thin films of fluorescent molecules [23-25] and locally aggregated conjugated polymer thin films [26-27], which has probed the local molecular orientation and interaction. Near-field fluorescence spectra collected photoluminescence from the nanometer-scale surface of films which are excited in the near-field ("illumination-collection mode") certainly reflect chemical properties only in the nanometer-scale top surface of films. Consequently, simultaneous use of near- and far-field fluorescence spectroscopy is expected to give new information on the aggregation states of cyanine dye molecules not only in the bulk but in the nanometer-scale top surface in their organization.

In this study, near-field fluorescence spectroscopy in conjunction with far-field fluorescence and Raman spectroscopy has been applied to investigate the aggregation states of NK3175 molecules in the depth direction in several kind of hybrid films consisted of NK3175 and SWN, which might provide new information on the mechanism of the photoinduced spectral change due to NK3175 for the above film. Near-field photoluminescence (PL) spectra along with far-field ones reveal that the aggregation states of NK3175 molecules in the top surface of the above film are different from those in the bulk, in contrast to the case in the other hybrid film prepared by the alternative method. This study is expected to demonstrate new application of simultaneous use of near- and far- field PL spectroscopy to the characterization of films in the depth direction, from a nanometer-scale top surface to the bulk.

2. Experimental

2.1. Materials

A cyanine dye of 2-[5-(1,3-dihydro-3,3-dimethyl-1-octadecyl-2H-indol-2-ylidene)-1,3-pentadienyl]-3,3-dimethyl-1-octadecyl-3H-indolium perchlorate (NK3175; Hayashibara Biochemical Labs., Inc.) was used without further purification (Figure 1). Cation-exchangeable clay, SWN (CO-OP Chemical Co., Inc.), was used as a host material. It is a type of hydrophilic smectite, and has good transparency in the visible region. The composition is $[(\text{Mg}_{2.67}\text{Li}_{0.33})(\text{Si}_4\text{O}_{10})(\text{OH})_2]\text{Na}_{0.33}$, and the cation exchangeable capacity (CEC) is c.a. $0.6 \text{ meq}\cdot\text{g}^{-1}$. Distilled and deionized water (conductivity $< 4 \times 10^{-6} \text{ S}\cdot\text{cm}^{-1}$) and ethanol (Wako Pure Chemical Industries Co. Inc., spectroscopic grade) were used as solvents for the preparation of the organic-inorganic hybrid films.

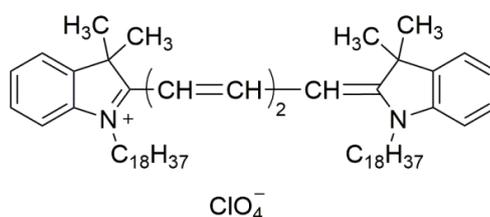


Figure 1. Chemical structure of cyanine dye of NK3175.

2.2. Preparation of the hybrid films

Solution of cyanine dye of NK3175 (1.5×10^{-6} mol) in ethanol (10 mL) added to aqueous suspensions of SWN (0.050 g/5mL) stirred at 60°C for 27 h in the dark. Aqueous suspensions of SWN were made by sonicating the mixture of SWN and deionized water for 60 min. or 5 min. Obtained viscous solutions were then casted on fused silica plates and dried at room temperature and transparent blue films were prepared. The obtained organic-inorganic hybrid films are, hereafter, referred to as NK3175-SWN(60min) and NK3175-SWN(5min). Another film of NK3175 and SWN, NK3175-SWN(dipping), was made by the alternative preparation method as follows. An aqueous suspension of SWN (0.020 g/5mL) was casted on a fused silica plate and dried at room temperature for 48 h and at 100°C for 3 h. Obtained SWN film was dipped in an ethanol solution of NK3175(1.5×10^{-4} M) at room temperature for 3.8 h, rinsed with ethanol, and dried at room temperature and a transparent blue film was prepared.

2.3. Measurement

Near- and far-field photoluminescence (PL) spectra were measured on near-field scanning optical spectrometer combined with microscopic optical spectrometer of NFS-230HGK (JASCO). Far-field Raman spectra were taken by laser Raman spectrometer of NRS-5100 (JASCO). An excitation wavelength of 532 nm produced by a Nd:YVO₄ laser was used for all far- and near-field measurement. The laser beam was produced a ca. 1 μ m diameter spot on the sample for far-field measurement, thus, spatial resolution could be roughly estimated to be ca. 1 μ m. Near-field PL measurement was performed in the illumination-collection mode and using double-tapered fiber probes with ca. 300, 180, 100, and 30 nm diameter apertures (JASCO Co., Inc.). According to previous reports [28-30] that the maximum spatial resolution of near-field scanning optical spectrometry (NSOM) is given by the diameter of the aperture, spatial resolution not only in horizontal direction but also in depth direction was supposed to be the aperture size of a fiber probe. Each near-field PL measurement was carried out without changing the measuring position of the sample which was set on far-field measurement. The near- and far-field PL profiles were reproducible and hardly changed from position to position and photodamage to the samples was not observed.

3. Results and discussion

3.1. Far-field Raman spectra of the hybrid films

Spectral change due to NK3175 in the visible region was occurred upon UV light irradiation in NK3175-SWN(60min) in agreement with our previous work [3], while that was hardly recognized in NK3175-SWN(5min) and NK3175-SWN(dipping). There might be a possibility that the comparison of the interaction between NK3175 and SWN and the aggregation states of NK3175 molecules among NK3175-SWN(60min), NK3175-SWN(5min) and NK3175-SWN(dipping) could give useful information on the mechanism of photoinduced spectral change in NK3175-SWN(60min). In the first place the far-field Raman measurement was performed for NK3175-SWN(60min), NK3175-SWN(5min) and NK3175-SWN(dipping). Figure 2 shows the far-field Raman spectra for the above hybrid films consisted of NK3175 and SWN and, for reference, the NK3175 powder. The observed bands at 1603, 1501, 1470, 1406, 1363 and 928 cm^{-1} for the above hybrid films (Figure 2a, 2b, and 2c) were in accord with those for NK3175 powder (Figure 2d), indicating that there are NK3175 molecules which did not participate in the chemical interaction with SWN such as adsorption in the above hybrid films. According to previous reports [31- 32], the band at 1603 cm^{-1} is assignable to C=N stretching motion of the end chromophore of NK3175 and the bands at 1470, 1406 and 1363 cm^{-1} might contain the contribution from the end chromophore vibration of NK3175. On the other hand, the new bands at 1556, 1433, 1300, 1173, 1124, and 1021 cm^{-1} appeared in the far-field Raman spectra for the above hybrid films, which is different from the far-field Raman spectrum for NK3175 powder (Figure 2d), and the bands at 1470 cm^{-1} for NK3175-SWN(60min) (Figure 2a) and NK3175-

SWN(5min)(Figure 2b) were relatively smaller than that for NK3175 powder. The XRD patterns of the above hybrid films in which the 100 reflection were observed around $d = 14.7 \text{ \AA}$ were almost similar to that of the SWN film in accord with our previous work [3], indicating that NK3175 molecules were not intercalated into SWN layers in the above hybrid films. These results are attributable to the adsorption of the cationic dye of NK3175 on the external anionic surface of SWN in agreement with our previous work [3], although the features of the above near-field Raman spectra do not seem to correspond to the photoinduced spectral behaviour for the above hybrid films. In Figure 2c the new bands at 1556, 1433, 1300, 1173, 1124, and 1021 cm^{-1} were relatively smaller than those in Figure 2a and 2b, suggesting that for NK3175-SWN(dipping) the number of NK3175 molecules adsorbed on SWN relative to NK3175 molecules which are independent of adsorption is smaller in comparison with that for NK3175-SWN (60min) and NK3175-SWN(5min). This might be originated from the difference in the preparation methods of these hybrid films. A possible explanation is as follows; for NK3175-SWN(60min) and NK3175-SWN(5min) NK3175 molecules and SWN were sufficiently mixed in liquid phase to result in the adequate adsorption of NK3175 molecules on SWN. On the contrary, in NK3175-SWN(dipping) there might be no appreciable chemical interaction between NK3175 molecules and SWN hardly to occur the adsorption of NK3175 molecules on SWN because of the introduction of NK3175 molecules not into the liquid phase but into the solid phase of SWN.

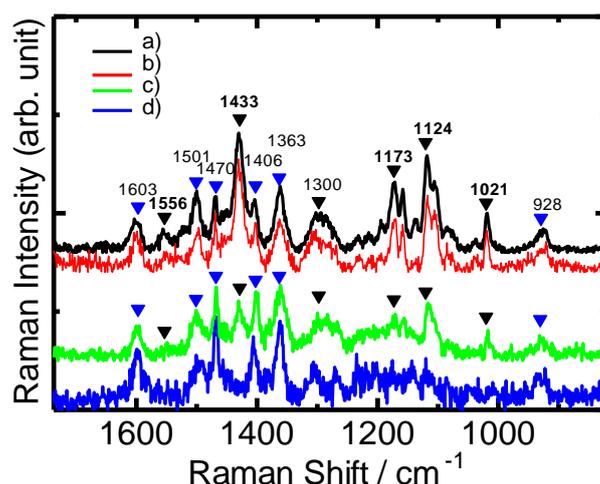


Figure 2. Far-field Raman spectra of a) NK3175-SWN(60min), b) NK3175-SWN(5min), c) NK3175-SWN(dipping), and d) NK3175 powder. ▼ indicates the bands observed for NK3175 powder, whereas ▲ indicates the newly observed bands for the above hybrid films.

3.2. Far-field PL spectra of the hybrid films

The position of the PL maxima is known to reflect the nature of the surrounding environment which affects aggregation states and is explained in terms of polar and/or rigid nature of the microenvironment. Figure 3 shows the far-field PL spectra of the hybrid films consisted of NK3175 and SWN and, for reference, the NK3175 film spin-coated from a THF solution of NK3175, referred to as NK3175 film. NK3175-SWN(60min) and NK3175-SWN(5min) exhibited their PL maxima around 700 nm with the shoulder-like structure around 650 nm, whereas for NK3175-SWN(dipping) the PL maximum was slightly red-shifted to ca. 709 nm and this band shape was rather unsymmetrical compared to that for NK3175-SWN(60min) and NK3175-SWN(5min). This unsymmetrical PL shape might be due to the self-absorption of the fluorescence of NK3175 molecules in NK3175-SWN(dipping). Consequently, the far-field PL spectra of NK3175-SWN(60min), NK3175-SWN(5min), and NK3175-SWN(dipping) are fundamentally similar to that of NK3175 film, which indicates that the aggregation states of NK3175 molecules roughly resemble in these films. The

electronic absorption spectra of NK3175-SWN(60min) [3], NK3175-SWN(5min), and NK3175-SWN(dipping) were similar to show the absorption bands around 650 and 603 nm probably ascribed to monomers and H-dimers of NK3175, respectively [10, 17], which is in accordance with the above far-field PL result that the aggregation states of NK3175 molecules approximately resemble in these films. It has been reported that the blue shift of the PL maximum indicates polarity and/or rigidity of the microenvironment of organometallic complex ions of $\text{Ru}(\text{bpy})_3^{2+}$ in the hybrid systems of these ions and inorganic layered materials [33]. From this fact and nonfluorescent ability of H-dimers, for NK3175-SWN(60min) and NK3175-SWN(5min) it could be assumed that the shoulder-like structure around 650 nm which was slightly appeared in the far-field PL spectra is blue-shifted from the PL maxima around 700 nm based on monomers of NK3175 and that this shoulder-like structure is possibly ascribed to the polar and/or rigid environment around NK3175 molecules. In analogy with the far-field Raman results, the features of the far-field PL and the electronic absorption spectra for the above hybrid films do not seem to correspond to their photoinduced spectral behaviour.

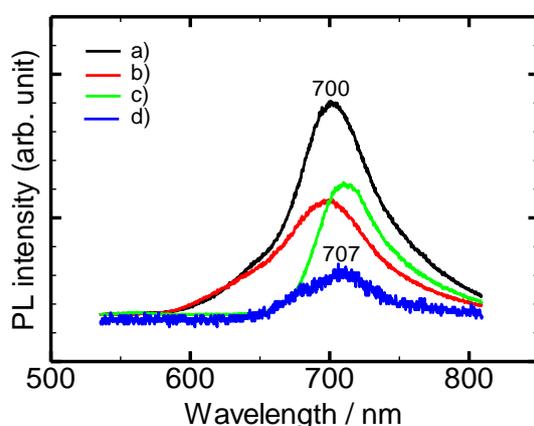


Figure 3. Far-field photoluminescence spectra of a) NK3175-SWN(60min), b) NK3175-SWN(5min), c) NK3175-SWN(dipping), and d) NK3175 film.

3.3. Near-field PL spectra of the hybrid films

The near-field PL spectra for NK3175-SWN(60min) and NK3175-SWN(5min) were dependent on the aperture diameters of fiber probes used on their measurement in contrast to those for NK3175-SWN(dipping). The features of near-field PL spectra for the above hybrid films do not seem to correspond to their photoinduced spectral behaviour as well. Further investigation should be needed in order to clarify the mechanism of the photoinduced spectral change in NK3175-SWN(60min). Figures 4, 5 and 6 show the near-field PL spectra for NK3175-SWN(60min), NK3175-SWN(5min) and NK3175-SWN(dipping), respectively. The observed near- and far-field PL maxima are summarized in Table 1. For NK3175-SWN(60min) the broad near-field PL maxima were observed around 700 nm in the use of fiber probes with ca. 300, 180, and 100 nm diameter apertures (Figure 4a, 4b, and 4c) and the fluorescent shoulder which might be correspond to the shoulder-like structure slightly appeared around 650 nm in its far-field PL spectrum (Figure 3a) was also observed around 650 nm in the use of a fiber probe with a ca. 300 nm diameter aperture (Figure 4a). These near-field PL profiles were nearly similar to the far-field PL spectrum of NK3175-SWN(60min). These results suggest that the aggregation states of NK3175 molecules in the inside more than ca. 100 nm from the top surface of NK3175-SWN(60min) are almost analogous to those in the bulk. On the other hand, the near-field PL maximum in the use of a fiber probe with a ca. 30 nm diameter aperture (Figure 4d) was significantly blue-shifted to ca. 649 nm and the half-value width of this band was relatively narrow compared to the near-field PL spectra taken by fiber probes with larger diameter apertures (Figure 4a, 4b, and 4c). This indicates that the aggregation states of NK3175 molecules in the outermost surface of NK3175-SWN(60min) within ca. 30 nm are different from those in the bulk and are somewhat limited. In this way it is demonstrated that the near-field PL spectra measured by using fiber probes with various aperture sizes together with the far-field ones give fruitful information on the aggregation states of

NK3175 molecules in NK3175-SWN(60min) not only in the bulk but in the top surface with the level of several tens of nanometers.

The near-field PL spectra for NK3175-SWN(5min) exhibited the similar tendency to those for NK3175-SWN(60min) that the aggregation states of NK3175 molecules in the outermost surface within ca. 30 nm of NK3175-SWN(5min) are different from those in the bulk. The broad near-field PL bands were observed around 694 nm by using fiber probes with ca. 300 and 180 nm diameter apertures (Figure 5a and 5b). On the other hand, the near-field PL maximum in the use of the fiber probe with a ca. 30 nm diameter aperture (Figure 5c) was considerably blue-shifted to ca. 649 nm and the half-value width of this band was relatively narrow compared to the near-field PL spectra taken by fiber probes with larger diameter apertures (Figure 5a and 5b). According to the previous report [33], it could be assumed that the polar and/or rigid environment around NK3175 molecules is greatly induced in the top surface of NK3175-SWN(60min) and NK3175-SWN(5min), leading to the blue shift in their near-field PL spectra. On the other hand, this kind of environment around NK3175 molecules is presumed to be slightly produced in the bulk of NK3175-SWN(60min) and NK3175-SWN(5min). It is well-known that the structure of a solid surface is generally different from that in the bulk and influences many of its important properties such as chemical and electronic properties. Accordingly, for NK3175-SWN(60min) and NK3175-SWN(5min) the arrangement of NK3175 molecules and SWN in the top surface could be somewhat different from that in the bulk. One of the possible situations is that there is more number of NK3175 molecules externally adsorbed on SWN in the top surface relative to those in the bulk of NK3175-SWN(60min) and NK3175-SWN(5min). In this case, the more polar and/or rigid microenvironment of NK3175 molecules could be caused in the top surface of these hybrid films, resulting in the blue-shifted photoluminescence.

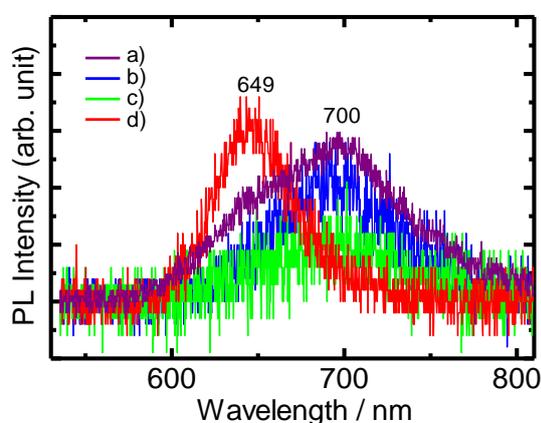


Figure 4. Near-field photoluminescence spectra of NK3175-SWN(60min) measured by using fiber probes with various opening diameters of a) 300 nm, b) 180 nm, c) 100 nm, and d) 30 nm.

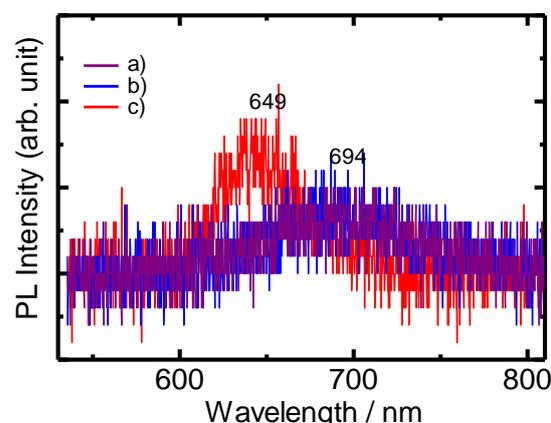


Figure 5. Near-field photoluminescence spectra of NK3175-SWN(5min) measured by using fiber probes with various opening diameters of a) 300 nm, b) 180 nm, and c) 30 nm.

On the other hand, the near-field PL spectra for NK3175-SWN(dipping) taken by using fiber probes with ca. 100 and 30 nm diameter apertures were similar. Moreover, these PL maxima at ca. 704 nm were comparable to the far-field PL spectrum of NK3175-SWN(dipping). These results indicate that the aggregation states of NK3175 molecules in the outermost surface within ca. 30 nm of NK3175-SWN(dipping) are in accordance with those in the bulk, in contrast to the cases in NK3175-SWN(60min) and NK3175-SWN(5min). These difference in the aggregation states of NK3175 molecules in the top surface between NK3175-SWN(dipping) and the other hybrid films of NK3175-

SWN(60min) and NK3175-SWN(5min) might come from the preparation method of these films, although the details of this origin are not clear.

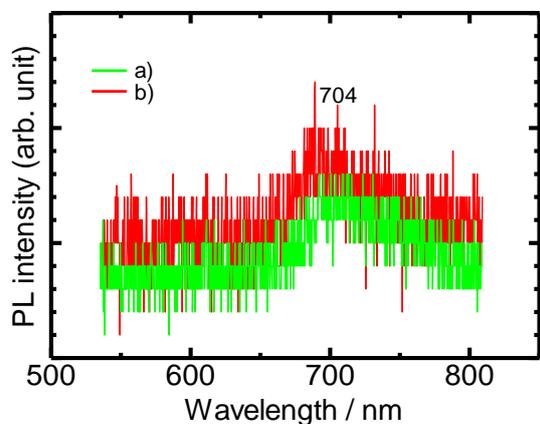


Figure 6. Near-field photoluminescence spectra of NK3175-SWN(dipping) measured by using fiber probes with opening diameters of a) 100 nm and b) 30 nm.

Table 1. Observed near- and far-field photoluminescence (PL) maxima for the hybrid films of NK3175 and SWN.

Samples	Observed PL maxima / nm				
	opening diameters / nm				diameter of a beam spot / μm
	30	100	180	300	1
NK3175-SWN (60min)	649	696	698	700	700
NK3175-SWN (5min)	649	-----	694	694	699
NK3175-SWN (dipping)	704	704	-----	-----	709

4. Conclusions

The aggregation states of NK3175 molecules in the hybrid films consisted of NK3175 and SWN, NK3175-SWN(60min), NK3175-SWN(5min) and NK3175-SWN(dipping), not only in the bulk but in the outermost surface within ca. 30 nm are demonstrated by simultaneous use of near- and far-field PL spectra. The aggregation states of NK3175 molecules in the outermost surface within ca. 30 nm of NK3175-SWN(60min) and NK3175-SWN(5min) are different from those in the bulk, in contrast to the case in NK3175-SWN(dipping) which was made by the alternative preparation method. The blue-shifted near-field photoluminescence for NK3175-SWN(60min) and NK3175-SWN(5min) suggests the top surface of these films to become more polar and/or rigid in terms of the microenvironment around NK3175 molecules relative to the bulk of them. These results are expected to show new application of simultaneous use of near- and far-field PL spectra to the characterization of films in the depth direction, from the top surface with the level of several tens of nanometers to the bulk. The far-field Raman spectra exhibit that the above hybrid films contained both NK3175 molecules which did not take part in the adsorption and those adsorbed on the external surface of SWN.

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