Unusual Spectral Change Due to a Cyanine Dye Adsorbed on an Inorganic Layered Material upon Photoirradiation

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Abstract
Photoinduced spectral change can be utilized for various optical devices. The photoinduced spectral change due to an organic dye was demonstrated for the organic-inorganic hybrid film without the aid of photochromism with a simple preparation method for the first time. By the hybridization of 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) with an inorganic layered material of cation-exchangeable clay, smectite (SWN), a spectral change attributed to NK3175 was generated upon the irradiation of UV light. This result might serve as useful information on the methodology to produce optically controlled function for photoresponsive systems. Furthermore, the hybrid film of SWN and NK3175 was characterized by the use of XRD and FT-IR measurements. NK3175 molecules adsorbed onto external surfaces of SWN were confined by oriented SWN. It was suggested that the enhanced intermolecular interaction between NK3175 molecules caused by the hybridization with SWN resulted in the change of the aggregation state of NK3175 upon the UV light irradiation, which accounts for the spectral change of NK3175.

Keywords
Photoinduced Spectral Change, Cyanine Dye, Clay, Hybrid Material

1. Introduction
Organic dyes have attracted much attention from both viewpoints of fundamental science and practical applica-

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tions such as memories, switching devices, electroluminescent devices, solar cells, optical filters, etc. Change of physical properties such as optical reflectance, refractivity, and fluorescence caused by photoirradiation for photo-functional organic dyes has been utilized for various optical devices. Inorganic layered materials such as clay minerals are widely utilized as host materials for functional organic-inorganic hybrid systems due to their characteristic properties of intercalation and adsorption of organic guest species [1]-[6]. Photo-functional organic-inorganic hybrid materials with an ordered structure have been constructed by utilizing intercalation and adsorption of photo-functional organic guest species into or on clay layers [1] [2] [7]. In such cases, distances between the photo-functional organic dyes become shorter. Therefore, it is expected that intermolecular interactions between these compounds are enhanced [1] [2] [8]. In fact, the intercalation and adsorption of the photo-functional organic dyes have enabled aggregation and alignment control of the organic dyes [1] [2] [8]-[14] and have affected photochemical properties, such as fluorescence behaviors [4] [5] [7] [8] [15]-[21].

The cooperative control of physical properties of the other organic material caused by an influence of photochromism is one of the active ways to create novel photo-functional systems [22]-[30]. Photochromic compounds have been extensively studied due to their possible application in various optical devices, such as memories and switches [31]. For photochromic memories one of the most pressing problems is on the method for non-destructive readout [31]. Monitoring change in ultraviolet (UV)-visible absorption is not a feasible method for non-destructive readout of photochromic memories; therefore, several alternative methods for non-destructive readout have been demonstrated [31]. On the other hand, photochromic compounds and organic dyes can be selected, so as to that the absorption of an organic dye and two isomers of a photochromic compound are in different spectral regions for the cooperative photoresponsive systems including these compounds. Accordingly there might be a possibility that monitoring change in the UV-visible absorption without an occurrence of a reverse photo isomerization reaction can be utilized for a non-destructive readout in this system. We proposed to monitor the absorption in the UV-visible region as a non-destructive readout method for a cooperative photoresponsive system and performed the photoinduced spectral change due to a cyanine dye by the use of a simple preparation method [30]. In order to amplify a cooperative effect of photochromism, we made use of an inorganic layered material together with an organic dye and a photochromic molecule to successfully prepare the hybrid film as a novel photo-functional organic-inorganic hybrid material [30]. It was shown that an electronic absorption spectrum ascribed to the cyanine dye was significantly changed by UV light irradiation for the hybrid film of the cyanine dye, a photochromic molecule of a diarylethene, and an inorganic clay mineral, smectite, [30]. However, the further mechanism of the photoinduced spectral change due to the cyanine dye for the above hybrid film is not elucidated. For the above hybrid film, smectite as well as the diarylethene is considered to play an important role in bringing about the photoinduced spectral change due to the cyanine dye. The interaction between the cyanine dye and smectite might affect the microstructure and the photoinduced spectral behavior for the above hybrid film.

In this study, we investigated the interaction between a cyanine dye and smectite and the photoinduced spectral behavior for the hybrid film of a cyanine dye and smectite. We demonstrate the interesting phenomena that without the aid of photochromism, a cyanine dye is induced to exhibit the photoresponsive property by hybridizing with an inorganic clay mineral, although a cyanine dye itself does not show any photoresponsive properties. This study is expected to give new information on the methodology to introduce optically controlled function for photoresponsive systems.

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 [(Mg$_{2.67}$Li$_{0.33}$)(Si$_4$O$_{10}$)(OH)$_2$]N$_{20.33}$, and the cation exchangeable capacity (CEC) is c.a. 0.6 meq·g$^{-1}$. Distilled and deionized water (conductivity < 4 × 10$^{-6}$ S·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.
2.2. Sample Preparation

Solution of cyanine dye of NK3175 (1.5 × 10⁻⁶ mol) in ethanol (10 mL) added to an aqueous suspension of SWN (0.050 g/5mL) and stirred for 27 h at 60°C in the dark. Obtained viscous solution was then casted on fused silica plates or Au-coated glass plates and dried at room temperature and transparent blue films were prepared. For FT-IR measurements, Au-coated glass plates were used. The obtained films are, hereafter, referred to as the hybrid films of SWN and NK3175. The ethanol solution of NK3175 (2.5 × 10⁻⁶ M) was also prepared for comparison.

2.3. Measurement

Electronic absorption spectra were recorded on a Shimadzu SolidSpec-3700 spectrophotometer. X-ray diffraction (XRD) patterns were measured with a RIGAKU RINT 2500 or a RIGAKU Smart Lab diffractometer using CuKα radiation source operating at 40 kV and 200 mA as the applied voltage and current, respectively. FT-IR spectra were measured on a Nicolet is 50 FTIR at 4 cm⁻¹ resolution. FT-IR reflection spectra of films were taken using a variable angle reflection accessory at an incident angle of 45 degrees. In the case of the measurement of polarized FT-IR spectra, a ZnSe polarizer was used. An attenuated total reflection (ATR) FT-IR spectrum of NK3175 powder was taken using Smart iTR accessory. UV light of around 254 nm (c.a. 1100 μW cm⁻²) was irradiated for 5 minutes using a handy UV lamp.

3. Results and Discussion

3.1. Spectral Change of the Hybrid Films of SWN and NK3175 upon Photoirradiation

Figure 2 shows electronic absorption spectra of the hybrid film of SWN and NK3175 before and after irradiation of UV light at 254 nm. For the solution of NK3175, the bands at 598 and 647 nm were observed (Figure 2(a)). These peaks were not changed by UV light irradiation at 254 nm. These bands could be ascribed to H-dimers and monomers of NK3175, respectively, according to the previous reports [8] [16] [32]. Before the UV light irradiation, the absorption bands at 603 and 652 nm ascribed to H-dimers and monomers of NK3175, respectively, were lightly red-shifted from those for the solution of NK3175, which were caused by adsorption of cationic NK3175 on negatively charged SWN [16]-[18] [33]. In addition, the relative intensity of the band at 603 nm to the band at 652 nm in the hybrid film in comparison with that in the solution of NK3175 increased, indicating that hybridization with SWN promotes the formation of H-dimers of NK3175.

On the other hand, it was interestingly found that in the hybrid film of SWN and NK3175 the spectral change due to NK3175 was occurred upon UV light irradiation at 254 nm. Upon the irradiation of UV light, the bands at 412 and 531 nm were clearly appeared, whereas the bands at 603 and 652 nm significantly decreased (Figure 2(c)). This change was essentially in good accord with our previous report which demonstrate a spectral change in the hybrid films of SWN, NK3175 and a diarylethene [30]. The change was somewhat smaller in this study probably because of the absence of the movement accompanied by a photochromic reaction [30]. The irradiated spectrum gradually returned to the one before UV light irradiation and reached a stationary state on keeping this film for about 23 h in the dark at room temperature, which indicates the observed spectral change do not arise from the photodecomposition of NK3175. Upon repeated irradiation of UV light, the similar spectral change took place as in the first time again. According to the previous report [8] [33], we presumed that the bands at 412 and 531 nm were ascribed to higher-order H-aggregates of NK3175 resulted from disaggregated H-dimers and monomers of NK3175. After UV light irradiation, after keeping this film in the dark the slow spectral change occurred for hours. It was reported that the aggregation of a cationic dye solution was instantly formed in...
the dispersions after mixing a cationic dye with a clay mineral, and then disaggregation of a cationic dye proceed slowly for hours and days [16] [34]. We assume that a similar situation occurs here. We have found that the similar spectral change due to other cyanine dyes, such as 2-[7-(1,3-dihydro-3,3-dimethyl-1-octadecyl-2H-indol-2-ylidene)-1,3,5-heptatrienyl]-3,3-dimethyl-1-octadecyl-3H-indolium perchlorate and 3-ethyl-2-[5-(3-ethyl-2(3-H)-benzoxazolylidene)-1,3-pentadienyl] benzoxazolium iodide also occurred upon UV light irradiation for the hybrid films with SWN.

3.2. Spectral Change of the Hybrid Film of SWN and NK3175 upon Heating

Figure 3 shows the electronic absorption spectra of the hybrid film of SWN and NK3175 on heating. Upon heating this film at 80°C for 1 h, the bands at 652 nm slightly shifted to 648 nm, which implies a change of a polar environment around NK3175 molecules [18] [35]. The spectral change such as the appeared bands at 531 and 412 nm and the decreased bands at 652 and 603 nm observed upon the UV light irradiation were not recognized upon heating. From these results, it was confirmed that the spectral change due to NK3175 upon UV light irradiation was caused not by heating but by photoirradiation.

3.3. X-Ray Diffraction and FT-IR Reflection Spectra of the Hybrid Film of SWN and NK3175

Figure 4 shows XRD patterns of the hybrid film of SWN and NK3175 and a casted film of SWN which was obtained from the suspension of SWN (0.051 g) in distilled and deionized water (5 mL) and ethanol (25 mL) stirred for 30 h at 60°C. The 100 reflections were observed at d = 14.7 Å (6.02 degree) and 14.2 Å (6.21 degree),
Figure 4. XRD patterns of a) the hybrid film of SWN and NK3175 and b) the casted film of SWN.

respectively. The slight enhancement of the d_{001} values indicates that NK3175 molecules were not intercalated into SWN layers.

FT-IR spectroscopy revealed the adsorption of a cationic dye of NK3175 on the anionic surface of SWN which appreciably oriented parallelism to the surface of the hybrid film of SWN and NK3175. Figure 5 and Figure 6 show the FT-IR spectra of the hybrid film of SWN and NK3175. In Figure 5(a), the bands at 1491, 1481, and 1456 cm\(^{-1}\) are assignable to the stretching vibration of the central conjugated system of NK3175. The bands at 1481 and 1456 cm\(^{-1}\) might contain a contribution from the in-plane skeletal vibration of the phenyl ring and a contribution from the CH\(_3\) asymmetric deformation vibration of NK3175, respectively [36]-[38]. The bands at 1491, 1481, and 1456 cm\(^{-1}\) were shifted and changed in relative intensity compared to those for NK3175 powder (Figure 5(b)). Moreover, the broad band around 1388 cm\(^{-1}\) and the band at 1335 cm\(^{-1}\) for the hybrid film (Figure 5(a)) were relatively smaller than those in NK3175 powder (Figure 5(b)). These bands are attributable to atomic motions in the methine chain of NK3175 and the band around 1388 cm\(^{-1}\) might contain a contribution from the CH\(_3\) symmetric deformation mode of NK3175 [36]-[38]. These were attributable to the adsorption of the cationic dye of NK3175 on the negatively charged external surface of SWN, which corresponds to the results from the electronic absorption spectra. Figure 6 shows the polarization dependency on the bands ascribed to the Si-O vibrations of SWN. In the \(p\)-polarized spectrum the bands at 1090 cm\(^{-1}\) and 977 cm\(^{-1}\) are assignable to the out-of-plane Si-O stretching and the in-plane Si-O stretching vibration of SWN, respectively. The band at 965 cm\(^{-1}\) observed in the \(s\)-polarized spectrum is attributable to the in-plane Si-O stretching vibration of SWN [33] [39]. These suggest that tetrahedral layers of SWN considerably oriented parallel to the surface of the hybrid film of SWN and NK3175 [30] [33] [39].

Taking into accounts the above results, one of the possible mechanism of the spectral change due to NK3175 induced by photoirradiation for the hybrid film of SWN and NK3175 is as follows; NK3175 molecules adsorbed onto the external surface of SWN are confined by the oriented SWN to approach each other. This situation is considered to enhance the intermolecular interactions between NK3175 molecules. Computational study for cyanine dyes previously reported that upon photoexcitation, the electron density on the methine chain increased, leading to the rotation of the methine chain [40]. For the hybrid film of SWN and NK3175, in a similar manner, upon photoirradiation the electron density on the methine chain of NK3175 somewhat increases, giving rise to the rotation of the methine chain, that is, the conformational change of NK3175. In the present case, NK3175 molecules approach each other so that they could strongly interact to form unique aggregation such as higher-order H-aggregates of NK3175 upon UV light irradiation. Consequently, the spectral change due to NK3175 is induced by photoirradiation for the hybrid film of SWN and NK3175. The spectral change due to NK3175 upon photoirradiation was enhanced in the hybrid film of SWN, NK3175 and the diarylethene [30] in comparison with that in the hybrid film of SWN and NK3175. It is probably because not only the above effect but also photochromism of the diarylethene which affected the state of aggregation of NK3175 have contributed to the enhanced spectral change upon photoirradiation in the hybrid film of SWN, NK3175 and the diarylethene [30].
4. Conclusion

The unusual spectral change ascribed to a cyanine dye was induced upon the irradiation of UV light without the help of photochromism, for the first time, by hybridizing a cyanine dye with an inorganic clay mineral with a simple preparation method. This result is expected to provide new information on the methodology to produce optically controlled function for photoresponsive systems. In addition, for the hybrid film of smectite of SWN and a cyanine dye of NK3175, it was suggested that NK3175 molecules adsorbed onto the external surface of SWN were confined by oriented SWN, enhancing the intermolecular interaction of NK3175 molecules, which induced the change of the state of aggregation of NK3175 upon UV light irradiation.

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