Monomeric Dispersion of Covalently Attached Pyrene Chromophores in Silylated Graphite Oxide

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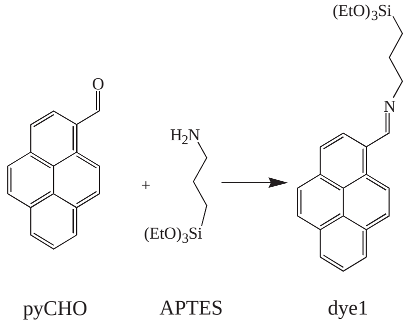
Pyrenecarboxaldehyde was covalently attached to the layer of silylated graphite oxide. Pyrene chromophore was almost monomerically dispersed in the resulting material with lower pyrene contents, because the aggregation of them was prevented by alkyl chains of silylated graphite oxide.

Recently, solid materials such as zeolites, mesoporous silicas, and layered compounds are attracting interest as matrices of photofunctional molecules for which the aggregation state and orientation are controlled.[1–3] In this context, we have reported that the aggregation and orientation of pyrene and rhodamine B molecules can be controlled in graphite oxides hydrophobized by cationic surfactant or alkylamines.[4,5] Potential applications of these materials include solid lasers in which dye molecules are dispersed in thin-film intercalation compounds at high concentrations without aggregation. However, the interaction between dye molecules and the above hydrophobized graphite oxides was weak and aggregation of dyes or loss of them was observed when they are left even in an ambient atmosphere. In order to overcome these problems, it is necessary to introduce dye molecules into layered materials via stronger interaction, for example, covalent bonding. For this study, therefore, pyrene chromophore was introduced via Si–O covalent bonding into graphite oxide silylated by alkyltrichlorosilane with long alkyl chains. It is also expected that the aggregation of pyrene chromophores is prevented by the "spacer" or "size matching" effect of alkyl chains.[6–9]

Graphite oxide (GO, $C_8O_{4.0}H_{3.0}$) was prepared from natural graphite powder (57–74 µm) by the method of Brodie. The alkyl groups were introduced into GO via Si–O covalent bonding using octadecyltrichlorosilane molecules in the same manner as reported in our previous papers.[10,11] A composition of $(C_{18}H_{37}SiOH)_{1.7}GO(C_4H_9NH_2)_{0.32}$ (hereafter abbreviated as C18Si–GO) was provided by elemental analysis. Introduction of 1-pyrenecarboxaldehyde was performed as follows: 1-Pyrenecarboxaldehyde (abbreviated as pyHCO, 463 mg) was first reacted with 3-aminopropyltriethoxysilane (abbreviated as APTES, 0.525 mL) in toluene (15 mL) at 60 °C for 1 day. The molar ratio of pyCHO and APTES was 1 : 1. A small amount of yellowish white precipitate was formed and it was removed by centrifugation. In the ^{1}H NMR (Bruker 500RX) spectrum of the yellow liquid product obtained after removing toluene, the peak at 10.83 ppm due to aldehyde proton of pyCHO completely disappeared and that of amino proton derived of APTES at 3.70 ppm quantitatively decreased. This strongly indicated the formation of dye **1** as shown in Scheme 1. The toluene solution of dye **1** was reacted with C18Si–GO (15 mg) at 110 °C for 1 day. The concentrations of dye **1** solution (15 mL) were varied between 2.9 and 43 mmol/L. The resulting samples were filtered off, washed with acetone several times, and then dried at 60 °C. The reaction of C18Si–GO (15 mg) with APTES (0.525 mL) was also performed for comparison. The obtained samples were analyzed by X-ray diffractometry (Rigaku Rint-2100, Cu Kα radiation), FT-IR (KBr method), TG measurement (Shimadzu TG50), and fluorescence spectroscopy (Hitachi F-2500, excitation wavelength: 330 nm). In the measurement of fluorescence spectroscopy, powder samples were pressed onto the quartz substrate.



Scheme 1. Preparation of dye **1**.

Figure 1 shows the X-ray diffraction patterns of pristine C18Si–GO and those reacted with dye **1** or APTES for 1 day. The diffraction peak at $2\theta = 3.84°$ (interlayer spacing of 2.30 nm) shifted to lower angle of 2.36° (interlayer spacing of 3.74 nm) for the samples reacted with dye **1** as shown in Figures 1C and 1D, indicating that the interlayer spacing increased by 1.44 nm. The interlayer spacing of the reaction product of C18Si–GO with APTES (Figure 1B) was almost similar to that of C18Si–GO reacted with dye **1**. However, the diffraction peak appeared at $2\theta = 2.08°$ (interlayer spacing of 4.25 nm) for the

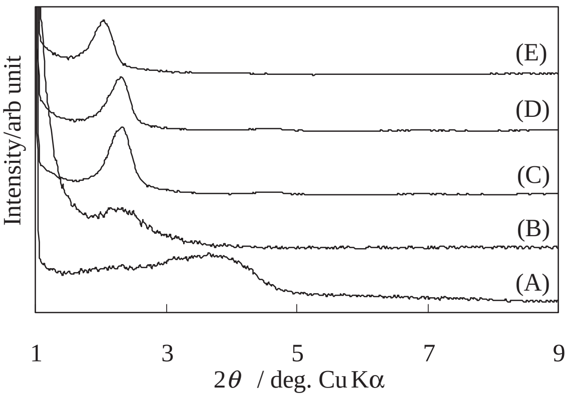


Figure 1. X-ray diffraction patterns of (A): C18Si–GO and those reacted with APTES: (B) and dye **1**: ((C)–(E)). The concentrations of dye **1** solution were (C): 2.9, (D): 8.7, and (E): 43 mmol/L.

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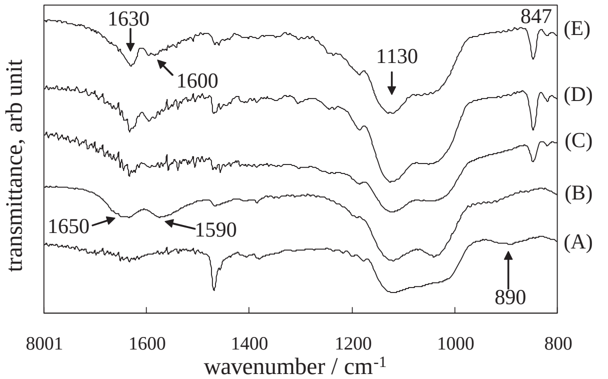

Figure 2. IR spectra of (A): C18Si–GO and those reacted with APTES: (B) and dye **1**: ((C)–(E)). The concentrations of dye **1** solution were (C): 2.9, (D): 8.7, and (E): 43 mmol/L.

sample obtained in the solution of 43 mmol/L (Figure 1E). The increase of interlayer spacing strongly suggests that the density of organic components including not only APTES but also dye **1** in the layer of C18Si–GO increased as the result of silylation of it by triethoxysilyl groups. Therefore, the pyrene chromophores are expected to locate in the spaces arising between alkyl chains in GO. In addition, note that no increase of interlayer spacing was observed when GO without alkyl chains was reacted with the dye **1** solution in the same manner. Exfoliation of the GO layers hydrophobized by long alkyl chains in toluene facilitated the access of dye **1** to the surface of them.

Figure 2 shows the IR spectra of C18Si–GO and those reacted with APTES or dye **1**. The absorption peaks at 847 and 1600 cm^{-1} which are ascribed to the vibration of aromatic C–H and benzene ring of pyrene chromophores, respectively, were observed. The relatively sharp absorption peak at 1630 cm^{-1} was due to the C=N vibration in dye **1**. These peaks were more clearly observed for the sample reacted with larger amounts of dye **1** and were absent in the spectrum of C18Si–GO reacted with APTES. The absorption peaks at 1650 and 1590 cm^{-1} in Figure 2B are due to ammonium type- and hydrogen bonded-amino groups of APTES.[12] The absorption peak at 890 cm^{-1} due to Si–OH group almost disappeared after the reaction with dye **1** or APTES and that at 1130 cm^{-1} derived of Si–O bonding became relatively stronger. This suggests that dye **1** mainly reacted with silanol group of C18Si–GO[11] and released some of the ethoxy group as ethanol. These X-ray and IR measurements indicate that dye **1** was introduced between the layers of C18Si–GO via Si–O bonding.

Figure 3 shows the emission spectra of C18Si–GOs reacted with dye **1**, together with that of dilute heptane solution of dye **1**. Two peaks at 394 and 417 nm were observed, together with a broad peak centered at 490 nm in the spectra of C18Si–GOs reacted with dye **1**. The peak positions of the former two peaks slightly shifted to longer wavelengths by 3 or 4 nm from those observed for dye **1** solution in heptane and they should be due to monomeric pyrene chromophore. When the amount of the added dye **1** increased, the broad peak at 490 nm became stronger; therefore, this peak is ascribed to the aggregated pyrene chromophores. This shows that pyrene chromophores were well isolated from each other by the spacer effect of long alkyl chains especially when the amount of pyrene existing between the layer of GO was low. Almost no change was observed in the emission spectra of the above samples when they are left under ambient atmosphere, which was in contrast with the case using graphite oxides hydrophobized by alkylamines as hosts of dye molecules such as pyrene or rhodamine B molecules. De-intercalation of alkylamines and aggregation of dye molecules gradually occurred for these samples. In addition to this, TG measurement of the sample (B) in Figure 3 showed negligible weight loss below 150 °C. The higher stability should be due to the stronger bonding between silylated GO and dye **1**. The hydrophobic nature of the silylated GO also prevented the penetration of water molecules which may hydrolyze dye **1** molecules bonded to GO layers.

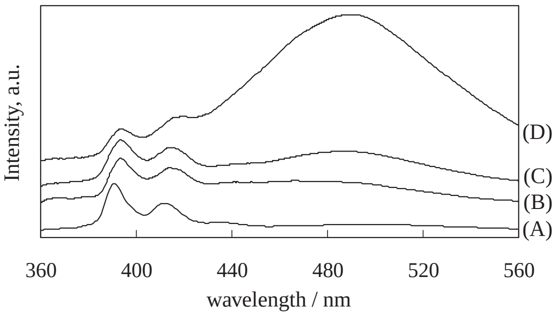

Figure 3. Fluorescence spectra of (A): dye **1** in heptane and C18Si–GO reacted with dye **1**: ((B)–(D)). The concentrations of dye **1** solution were (B): 2.9, (C): 8.7, and (D): 43 mmol/L.

The elemental analysis of the sample prepared in the dye **1** solution of 2.9 mmol/L showed that it contained 64.13% of carbon, 6.41% of hydrogen and 3.86% of nitrogen. The silicon content was determined from the weight of the residual SiO_2 after TG measurement and 9.84% was obtained. Assuming that all the changes in composition during the reaction between C18Si–GO and dye **1** were ascribed to the uptake of dye **1**, the Si content appeared too much. This may indicate that APTES which existed in dye **1** solution also included in this material.

In conclusion, pyrene chromophores were successfully introduced into GO via Si–O bonding and thermally and chemically stable products were obtained. By reducing the amount of introduced pyrene chromophores, they were well separated from each other and the emission from monomeric pyrene became dominant. This material would be promising for the solid dye laser.

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