Monomer emission from pyrene adsorbed in surfactant-intercalated graphite oxide

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Monomer emission from pyrene highly concentrated in octadecyltrimethylammonium ion-intercalated graphite oxide has been observed.

Organoammonium ion-intercalated layered materials have attracted much attention because of their interesting structure, absorption of harmful molecules or photoactive ones and application as catalysts. Studies on these materials have been well summarized recently by Ogawa and Kuroda.[1] Among these studies, interesting results on fluorescence, thermal properties or photo-isomerization have been reported by immobilizing photochromic molecules such as pyrene,[2,3] azobenzene,[4,5] spiropirane,[6] *etc*., in the two dimensional space of intercalation compounds. On the other hand, we have found that graphite oxide (GO) which is classified as a covalent type of graphite intercalation compound allows formation of intercalation compounds with alkyltrimethylammonium ions and the maximum content of surfactant in the layer is very large compared with that of clays and covers a wide range.[7] Such intercalation compounds of GO are easily dispersed in chloroform, which can lead to further intercalation of aromatic molecules by casting the solution containing both the intercalation compound and guest molecules. These facts suggest that it is possible to control the adsorption state of photochromic molecules in the two dimensional space of surfactant-intercalated GO over a wide range by changing the size of the spacing between the alkyl chains of surfactant.

In this study, we chose pyrene as a probe photochromic molecule in order to characterize the surfactant-intercalated GO as a new host material for photochromic molecules. The aggregation state of pyrene was analyzed by using X-ray diffraction and fluorescence spectra as was used for the characterization of pyrene in montmollironite.[2,3]

Graphite oxide ($C_8O_{3.5}H_{2.8}$) was obtained from natural graphite powder by a modified Staudenmaier method.[8,9] Oxidation of graphite was carried out for 2 days. Intercalation of octadecyltrimethylammonium ion ($C_{18}H_{37}Me_3N^+$; $C_{18}3C_1N$) and dimethyldioctadecyl ammonium ion [$(C_{18}H_{37})_2Me_2N^+$; $2C_{18}2C_1N$] was performed by adding an aqueous solution of surfactants to a colloidal solution of GO.[7] The repeat distance along the *c*-axis (I_c) of surfactant of $C_{18}3C_1N$- and $2C_{18}2C_1N$-intercalated GO as hosts of pyrene were 3.25 and 3.11 nm, respectively. The contents of surfactant in GO were 0.33 and 0.23 mol per 100 g of GO in these intercalation compounds when calculated from weight uptake data. These values are very large when compared with those of clay minerals. The samples obtained in this study were highly soluble in chloroform. Intercalation of pyrene was performed by casting from $CHCl_3$ solution (5 ml) containing the intercalation compound (10 mg) and pyrene (2.5, 3.3 or 5.0 mg) on a quartz substrate. X-Ray diffraction was performed on a Rigaku Rint-2100 diffractometer. Absorption and luminescence spectra were recorded on a Hitachi U-3000 spectrometer and JASCO FP-777 spectrofluorometer at an excitation wavelength of 330 nm, respectively.

Casting of a $CHCl_3$ solution containing surfactant-intercalated GO and pyrene gave slightly brownish transparent films for all the samples. Fig. 1 shows the X-ray diffraction patterns of the cast films of PY-$C_{18}3C_1N$-GO, PY-$2C_{18}2C_1N$-GO, $C_{18}3C_1N$-GO and $2C_{18}2C_1N$-GO, together with that of pristine GO. In both cases, the I_c values of surfactant-intercalated GO increased to about 3.8 nm after the addition of pyrene, indicating the intercalation of pyrene into the surfactant-intercalated GO materials. These I_c values were similar to those observed for pyrene-$C_{18}3C_1N$- or pyrene-$2C_{18}2C_1N$-montmorillonites.[2] They were almost constant regardless of the amount of added pyrene. When the weight ratio of surfactant-intercalated GO to pyrene was $> 1 : 0.5$, a diffraction peak at $2\theta = 10.3°$ appeared in the diffractogram of both PY-$C_{18}3C_1N$-GO and PY-$2C_{18}2C_1N$-GO, probably due to saturation of pyrene in the interlayer spacing of the intercalation compounds and crystallization of excess pyrene at the surface of the samples. The molar ratios of pyrene : $C_{18}3C_1N$ and pyrene : $2C_{18}2C_1N$ are *ca*. 1 : 1 and 2 : 1, respectively, when pyrene is saturated in the layers of the intercalation compounds. In other words, saturation of pyrene occurred when the ratio of pyrene : octadecyl group was *ca*. 1 : 1.

Fig. 2 shows the UV absorption spectra of cast films of PY-$C_{18}3C_1N$-GO, PY-$2C_{18}2C_1$-GO, a pyrene film and an ethanolic solution of pyrene. In the absorption spectra of cast films of intercalation compounds containing pyrene, absorption bands due to $\pi–\pi^*$ transitions of pyrene were observed at 340, 324, 312, 275, 264, 243 and 235 nm. For pyrene in ethanolic solution, absorption bands were observed at 334, 318, 305, 272, 261, 240 and 230 nm. The red shift (*ca*. 5 nm) of absorption bands indicated that pyrene in GO interlayers is present in a more polar environment than in ethanolic solution.

Fig. 3 shows the fluorescence spectra of PY-$C_{18}3C_1N$-GO, PY-$2C_{18}2C_1$-GO, an ethanolic solution of pyrene and crystalline pyrene. It is well known that the emission bands observed at *ca*. 390 and 450 nm arise from pyrene monomer and eximer,
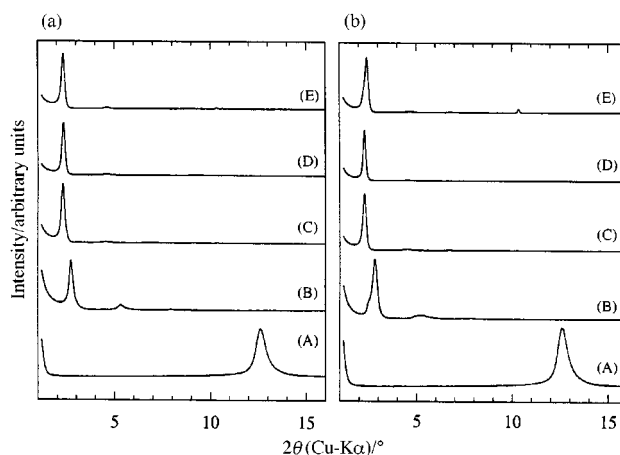

Fig. 1 (a) X-Ray diffraction patterns of (A) GO, and cast films of (B) $C_{18}3C_1N$-GO and of PY-$C_{18}3C_1N$-GO with $C_{18}3C_1N$-GO : pyrene ratios; (C) 1 : 0.25, (D) 1 : 0.33 and (E) 1 : 0.5. (b) X-Ray diffraction patterns of (A) GO, and cast films of (B) $2C_{18}2C_1N$-GO and of PY-$2C_{18}2C_1N$-GO with $2C_{18}2C_1N$-GO : pyrene ratios; (C) 1 : 0.25, (D) 1 : 0.33 and (E) 1 : 0.5.
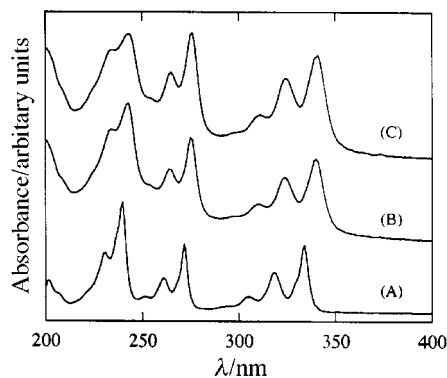
Fig. 2 The absorption spectra of (A) an ethanolic solution of pyrene, (B) PY-$C_{18}3C_1N$-GO with a $C_{18}3C_1N$-GO:pyrene ratio of 1:0.25 and (C) PY-$2C_{18}2C_1N$-GO with a $2C_{18}2C_1N$-GO:pyrene ratio of 1:0.25.
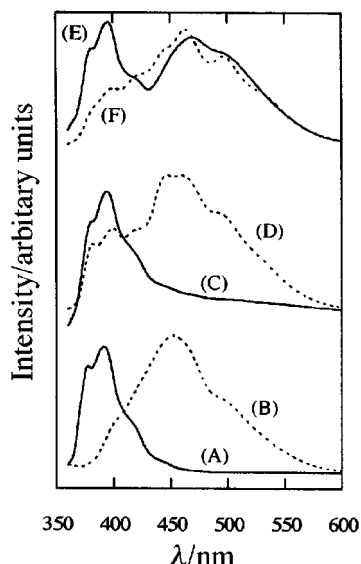

Fig. 3 The emission spectra of (A) crystalline pyrene, (B) an ethanolic solution of pyrene, and of PY-$C_{18}3C_1N$-GO with $C_{18}3C_1N$-GO:pyrene ratios of (C) 1:0.25 and (D) 1:0.33 and PY-$2C_{18}2C_1N$-GO with $2C_{18}2C_1N$-GO:pyrene ratios of (E) 1:0.25 and (F) 1:0.33.

respectively. The emission from the monomer is usually observed only in highly dilute solutions as shown in Fig. 3(A).

However, in the spectra of intercalation compounds with very high pyrene content, this line was observed clearly and its relative intensity increased when the loaded amount of pyrene was decreased. Moreover, it is noteworthy that almost no emission from the eximer was observed for PY-$C_{18}3C_1N$-GO (1:0.25), indicating that pyrene molecules in the layer are almost completely separated from each other by alkyl chains of surfactants. This would be because the high content of surfactant in the layer of GO makes the size of single pyrene molecules suitable to occupy the space present between alkyl chains of the surfactant. On the other hand, for PY-$2C_{18}2C_1$-GO, eximer emission was preferably observed even when the pyrene content was similar to that of PY-$C_{18}3C_1N$-GO showing monomer emission. Similar results on the change of aggregation state of pyrene were reported for montmorillonite based compounds;[2] however, in the latter case, the ratio of pyrene to surfactant chain was rather lower, at most 1:0.36, and eximer emission was observed to a considerable extent. The difference of emission spectra of the two intercalation compounds would be due to the difference of the size of the sites for pyrene adsorption.

Finally, we would like to emphasize that these surfactant-intercalated graphite oxides are suitable host materials for including photochromic molecules in separated sites at a very high concentration. It would be possible to control their aggregation over a wide range by changing the size of the spaces between the alkyl chains of the surfactants.

Notes and references

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