Chemistry Letters Vol.38, No.12 (2009)

Covalent Attachment of Pyrene onto the Layer Surfaces of Silylated Magadiite at a High Concentration without Aggregation

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(Received July 21, 2009; CL-090680; E-mail: ymatsuo@eng.u-hyogo.ac.jp)

Magadiite containing covalently attached pyrene chromophores at a high concentration was prepared by the reaction between silylated magadiite possessing amino groups and 1-pyrenebutanoic acid succinimidyl ester. The monomeric pyrene content without aggregation reached a very high value of 0.57 pyrene/nm^2 in the nanosheet state.

The immobilization of dye molecules without aggregation in solid matrices is an important issue for the application of the resulting materials to photochemical reaction media, solid dye laser, sensor, and artificial photosynthesis. In this context, several attempts have been made in order to increase the amount of the dyes introduced into layered materials as monomers. Incorporation of a third component into the interlayer spacing of clay or other layered materials as a spacer, together with dye molecules has been proposed by many researchers.[1,2] For example, the coadsorbed spacer ions with long alkyl chains effectively suppress the aggregation of dye molecules and for Rhodamine 6G (R6G)/surfactant-co-intercalated montmorillonite system, 0.04 R6G molecules/nm^2 without aggregation has been reported, when 1.6 nm^2 was used for the area per charge site of montmorillonite in the solid state.[2] On the other hand, the high loading of monomeric porphyrin on a layer of clay has been reported base on a size matching rule. A large value of 0.15 porphyrin molecules/nm^2 without aggregation has been achieved in the nanosheet state.[3] The separation distances between the adjacent anionic sites in the clay and between the adjacent cationic charges in the porphyrin molecules were made approximately equal. This method is effective only for dyes with appropriate sizes, charges, or shapes. In this context, we have reported covalent attachment of monomeric pyrene to graphite oxide layers. The spacer molecules were first attached by using silylating reagents, and then pyrene with triethoxysilyl groups was reacted.[4] In the subsequent paper, amino groups as adsorption sites for dyes were attached to the spacer molecules on magadiite, and then dye molecules were introduced into the resulting materials by using a succinimidyl ester containing pyrene chromophore which selectively reacts with amino groups.[5] However, aggregation was not perfectly suppressed, probably because it is difficult for the bulky dye molecules to diffuse between the layers of silylated layered materials when they are reacted with powder or film samples, preventing the uniform distribution of the attached dye. Moreover, it was difficult to determine the amount of attached dyes because it was too low to estimate. Therefore, in this study, the reaction was performed between nanosheets of silylated magadiite possessing amino groups and dye molecules in order to achieve uniform distribution of dyes and attachment of them at a high concentration. Then, the aggregation of pyrene chromophores was avoided by dispersing the resulting material in chloroform.

Magadiite ($Na_2Si_{14}O_{29}\cdot nH_2O$, abbreviated as Mag) was prepared, according to the literature.[6] Dodecyltrimethylammomium–Mag (abbreviated as C_{12}TMA–Mag) was prepared by mixing Mag (3 g) and an aqueous solution of dodecyltrimethylammomium chloride (0.1 M, 200 mL). The C_{12}TMA–Mag (150 mg) was silylated with docosyltrichlorosilane (hereafter C_{22}Si; 1 mL) in cyclohexane (10 mL) at 60 °C for 2 days. The silylated product was centrifuged, washed with acetone, and dried at 60 °C. The resulting silylated Mag (abbreviated as C_{22}Si–Mag; 60 mg) and 3-aminopropyltriethoxysilane (hereafter APS; 1.2 mL) were put in cyclohexane (30 mL) and were reacted at 80 °C for 1 day. The product was centrifuged, washed with cyclohexane and acetone, and dried at 60 °C. The resulting sample (denoted as APS–C_{22}Si–Mag; 8 mg) was dispersed in a chloroform solution of 1-pyrenebutanoic acid succinimidyl ester (PyBA-S; 4 mL, 1 mM) and sonicated. After reacting at 60 °C for 1 h, the product was centrifuged and washed with DMF and then cyclohexane. The sample was then dried under vacuum and was analyzed by X-ray diffraction (Rigaku Rint-2100, Cu Kα radiation), thermogravimetric analysis (TGA-50 Shimadzu, under air with a temperature increasing rate of 5 °C min^{-1}), UV–vis (Hitachi U-3010), and fluorescence spectroscopy (Hitachi F-7000, excitation wavelength of 330 nm).

Figure 1 shows the X-ray diffraction patterns of C_{22}Si–Mag, APS–C_{22}Si–Mag, and that reacted with PyBA-S. The diffraction peak at $2\theta = 2.96°$ ($d = 2.98$ nm) observed for C_{22}Si–Mag shifted to a lower angle of $2\theta = 2.32°$ ($d = 3.81$ nm) after reaction with APS, indicating the silylation of C_{22}Si–Mag and the successful introduction of amino groups. When the APS–C_{22}Si–Mag was reacted with PyBA-S, the diffraction peak shifted to a lower angle of $2\theta = 1.98°$ ($d = 4.46$ nm). This indicates that the density of the organic component in the layer spacing of APS–C_{22}Si–Mag increased most likely due to the introduction of pyrene chromophores and that alkyl groups took more perpendicular orientation against the layer of Mag. These indicate the covalent attachment of pyrene to the layers of APS–C_{22}Si–Mag via amide bonding.[4]

In the thermogravimetric analysis data of C_{22}Si–Mag, APS–C_{22}Si–Mag, and APS–C_{22}Si–Mag reacted with PyBA-S (Figure S1),[7] the weight decrease around 250 °C is due to the elimination of organic components such as APS and C_{22}Si. For pyrene-attached APS–C_{22}Si–Mag the weight decreased around 500 °C, which is attributed to the decomposition of pyrene. Based on the weight decrease due to these organic components, the contents of C_{22}Si, APS, and pyrene were determined, and the composition of

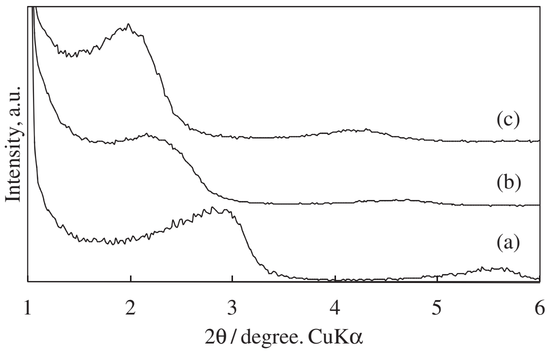

Figure 1. X-ray diffraction patterns of (a) C_{22}Si–Mag, (b) APS–C_{22}Si–Mag, and (c) APS–C_{22}Si–Mag reacted with PyBA-S (1 mM).

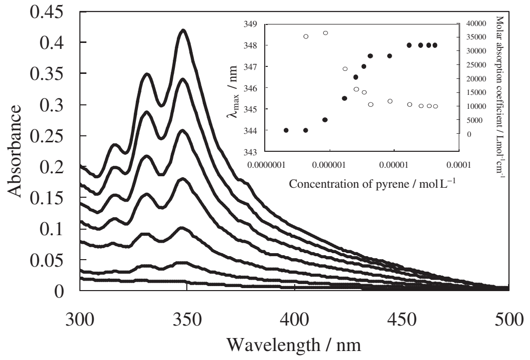

Figure 2. UV–vis absorption spectra of $(\mathrm{pyrene})_{0.38}\mathrm{APS}_{0.8}(\mathrm{C}_{22}\mathrm{Si})_{2.1}$-$\mathrm{Si}_{14}\mathrm{O}_{29}$ nanosheet solutions at various concentrations of 0.220, 0.176, 0.132, 0.088, 0.044, 0.022, and 0.0022 mg mL^{-1} from top to bottom. The inset shows the variation of the absorption maxima: ○ and molar absorption coefficient: ● of $(\mathrm{pyrene})_{0.38}\mathrm{APS}_{0.8}(\mathrm{C}_{22}\mathrm{Si})_{2.1}\mathrm{Si}_{14}\mathrm{O}_{29}$ at the absorption maxiuma as a function of the concentration of pyrene.

the resulting sample was $(\mathrm{pyrene})_{0.38}\mathrm{APS}_{0.8}(\mathrm{C}_{22}\mathrm{Si})_{2.1}\mathrm{Si}_{14}\mathrm{O}_{29}$. This pyrene content is much higher than that reported in our previous study.[5] It corresponds to 0.57 pyrene/nm^2 and 1.2-nm distance between two adjacent pyrene chromophores, assuming the homogenous distribution of pyrene and using the in-plane lattice parameter of Mag of $a = b = 0.73$ nm.[8] Considering the molecular length of pyrene chromophores, the aggregation of pyrene chromophores is expected to occur, and actually excimer fluorescence at 460 nm was strongly observed as shown in Figure S2.[7] The spacer effect is not strong enough to avoid the aggregation of pyrene in the solid state, probably because the interaction between alkyl chains and aromatic rings of pyrene chromophores was weaker than that between aromatic rings of pyrene chromophores.

The X-ray diffraction pattern of the chloroform slurry of pyrene-attached APS–C_{22}Si–Mg showed no diffraction peak as shown in Figure S3.[7] Moreover, when it was dispersed in chloroform, transparent homogenous solution was obtained, indicating the complete exfoliation of the pyrene-attached APS–C_{22}Si–Mg layers and the formation of nanosheet solution. Figure 2 shows the absorption spectra of the nanosheet solutions of the above sample at various concentrations. Three characteristic peaks due to pyrene chromophores were clearly observed at around 348, 329, and 314 nm and the absorption decreased with the decrease of the concentration. Inset shows the variation of the absorption maxima and molar absorption coefficient which was calculated by dividing the absorbance at the absorption maxima and optical path length of 1 cm as a function of the concentration of pyrene. Both started to change when the concentration of pyrene reached 10^{-5} mol L^{-1} and became almost constant below 10^{-6} mol L^{-1}. This indicates that the aggregated pyrene chromophores started to disaggregate around 10^{-5} mol L^{-1} and that disaggregation was completed around 10^{-6} mol L^{-1}. In other words, all the pyrene chromophores are aggregated above 10^{-5} mol L^{-1} and are monomers below 10^{-6} mol L^{-1}. Therefore, the molar absorption coefficients of monomeric and aggregated pyrenes are determined to be about 36000 and 20000 L mol^{-1} cm^{-1}, respectively. Here, note that the molar absorption coefficient for the aggregated pyrene was obtained by multiplying that at 10^{-5} mol L^{-1} by 2, assuming that the pyrene dimers were formed and that the concentration of them was half of that of the attached pyrene. The red shift of the absorption maximum of 4 nm and these molar absorption coefficients were almost the same as those reported for the pyrene attached to polymer in an aqueous solution.[9] This indicates that the pyrene chromophores were aggregated in the ground state at higher concentrations and that they were gradually disaggregated as the concentration of pyrene decreased. This idea is supported by the fluorescence spectra at various concentrations as shown in Figure 3. At higher concentrations, the broad fluorescence peak at 465 nm due to pyrene excimer was clearly observed; however, at a lower concentration, this almost disappeared and only the fluorescence peaks at 378 and 396 nm from pyrene monomer was observed. The value of 0.57 pyrene/nm^2 without aggregation is larger than those reported previously.[2,3] This was because the interaction between chloroform and pyrene was enough strong to disaggregate pyrene chromophores, especially when higher amounts of solvent were added.

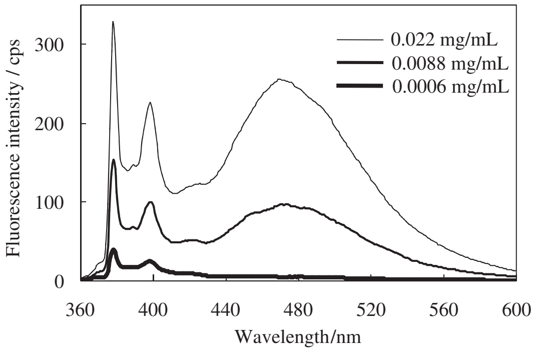

Figure 3. Fluorescence spectra of $(\mathrm{pyrene})_{0.38}\mathrm{APS}_{0.8}(\mathrm{C}_{22}\mathrm{Si})_{2.1}\mathrm{Si}_{14}\mathrm{O}_{29}$ nanosheet solution at various concentrations of 0.022, 0.0088, and 0.0006 mg mL^{-1}.

In conclusion, pyrene chromophores are attached to the layers of silylated magadiite containing amino groups at a high concentration by the reaction of the nanosheets of it with 1-pyrenebutanoic acid succimidyl ester. The monomeric pyrene content without aggregation reached very high value of 0.57 pyrene/nm^2 in the nanosheet state. We believe that the present method to attach monomeric dye molecules to the layered materials at a high density on each layer would be very useful for future applications.

References and Notes

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Published on the web (Advance View) October 31, 2009; doi:10.1246/cl.2009.1130