Journal of Fluorine Chemistry 129 (2008) 1150–1155

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Preparation of silylated magadiite thin-film-containing covalently attached pyrene chromophores

Y. Matsuo [a,*], Y. Yamada [a], M. Nishikawa [a], T. Fukutsuka [b], Y. Sugie [a]

[a] *Department of Materials Science and Chemistry, Graduate School of Engineering, University of Hyogo, 2167 Shosha, Himeji, Hyogo 671-2210, Japan*
[b] *Department of Interdisciplinary Environment, Kyoto University, Yoshida-nihonmatsu-cho, Sakyo-ku, Kyoto 606-8501, Japan*

ARTICLE INFO

Article history:
Received 5 August 2008
Received in revised form 27 August 2008
Accepted 28 August 2008
Available online 10 September 2008

Keywords:
Perfluoroalky groups
Magadiite
Silylation
Thin-film
Nanosheet
Pyrene
Fluorescence

ABSTRACT

Thin-film of magadiite (Mag) silylated by [2-(perfluorohexyl)-ethyl]trichlorosilane was prepared by casting the chloroform/ethylacetate nanosheet solution of it. The addition of alkylamine and perfluoroalkyl groups to silylated magadiite greatly changed the surface morphology of the resulting sample and the transparent thin-film with relatively smooth surface was obtained. Amino groups were introduced into it by using 3-aminopropyltriethoxysilane after removal of alkylamine. The reaction of 1-pyrenebutanoic acid succimidyl ester with the thin-film of silylated magadiite-containing amino groups in *N*,*N*-dimethylformaide (DMF) resulted in the covalent attachment of pyrene chromophores to it.

1. Introduction

Recently, solid matrices such as zeolites mesoporous silicas and layered materials are attracting much interest as matrices of photo-functional molecules [1–5]. The resulting materials are promising for solid dye laser, non-linear optics, etc. In this context, we have reported that it was possible to disperse organic dyes in hydrophobized-layered materials at high concentrations without aggregation and to control the orientation of them [6,7]. When perfluoroalkyl groups are introduced into them for hydrophobization instead of alkyl groups, due to the lower probability of vibrational excitation of C–F than that of C–H, radiationless quenching of the emission from dyes in them is greatly suppressed [6]. More recently, we have found that pyrene chromophores were covalently attached to the layers of graphite oxide silylated by alkyltrichlorosilane with a long alkyl chain by reacting it with pyrene chromophore possessing triethoxysilyl group [8]. This method is very useful in order to disperse dye molecules without aggregation and to obtain stable materials. It would be very nice to obtain similar materials from silica-based layered hosts in the state of thin-film, because they are transparent and accordingly more suitable for optical applications. It is also desirable to use more generally available dyes than those with triethoxylsilyl groups.

In this study, therefore, thin-film of silylated magadiite (Mag) containing perfluoroalkyl groups was first prepared by casting nanosheet solution of it on substrates. The effect of perfluoroalky groups and alkylamine added to the silylated magadiite on the surface morphology of the thin-film was investigated. Here, magadiite is one of the layered silicas and the composition of it is $Na_2Si_{14}O_{29}\cdot nH_2O$ [9–12] which is more transparent than graphite oxide in the region visible of light and silylation of magadiite have been also reported by several groups [13–21]. Then, amino groups were introduced into the resulting silylated magadiite thin-film and the pyrene chromophores were covalently attached to it by using succinimidyl ester of 1-pyrenebutanoic acids shown in Fig. 1 which is one of the DNA probe molecules and selectively reacts with amino groups [22,23].

2. Results and discussion

2.1. Preparation of silylated magadiite thin-film-containing perfluoroalkyl groups

Fig. 2 shows the X-ray diffraction patterns of Mag, C8FSi-Mag, C16-C8FSi-Mag powder, C16-C8FSi-Mag thin-film and C8FSi-Mag samples. The diffraction peak appeared at 5.6° for Mag shifted to

---

* Corresponding author. Tel.: +81 79 267 4898; fax: +81 79 267 4898.
E-mail address: ymatsuo@eng.u-hyogo.ac.jp (Y. Matsuo).

0022-1139/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2008.08.006

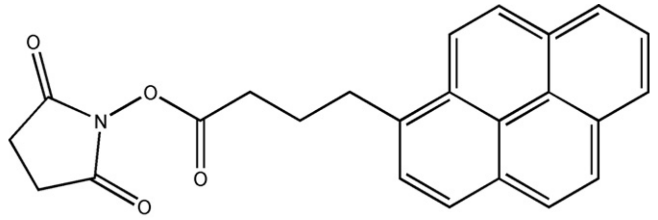


Fig. 1. Molecular structure of 1-pyrenebutanoic acid succinimidyl ester.

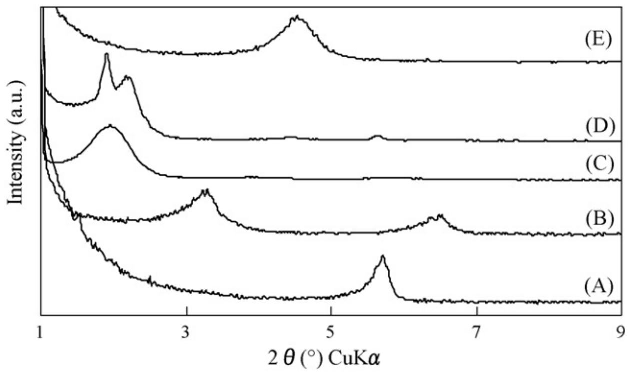


Fig. 2. X-ray diffraction patterns of (A) Mag, (B) C8FSi-Mag, (C) C16-C8FSi-Mag powder, (D) C16-C8FSi-Mag thin-film and (E) C16-C8FSi-Mag thin-film after refluxed in toluene.

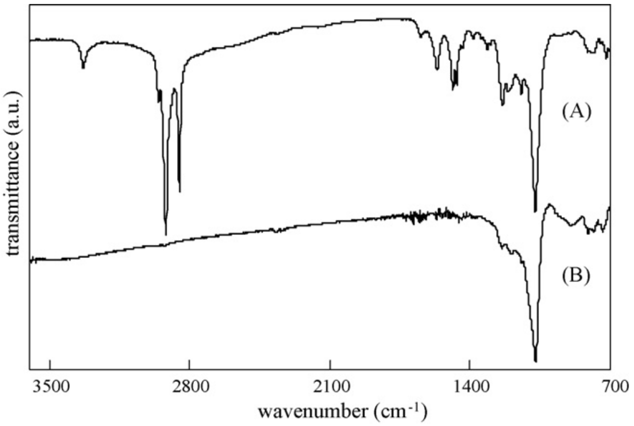


Fig. 3. IR spectra of C16-C8FSi-Mag thin-films (A) before and (B) after refluxed in toluene.

lower angle by exchanging sodium ion with C12TMA with long alkyl chains as reported by the literatures [18–21]. When C12TMA-Mag was reacted with C8FSi, the diffraction peak slightly shifted to higher angle of 3.30° as shown in Fig. 2(B), suggesting the successful silylation of Mag by C8FSi with shorter perfluoroalkyl chains and the interlayer spacing was 2.68 nm. Upon the introduction of C16 molecules into C8FSi-Mag powder, broad peaks appeared at $2\theta = 1.96°$, 3.92° and 5.74°, indicating the intercalation of C16 molecules and a layered structure with an interlayer spacing of 4.5 nm. The obtained C16-C8FSi-Mag powder was well dispersed in some solvents such as chloroform and ethylacetate, providing transparent solutions. It has been reported that transparent dispersion of hydrophobized layered materials is obtained when the refractive index of them are similar to that of the solvent or they are delaminated to the individual layers [21,24,25]. In the present case, transparent dispersion was commonly formed in solvents with different refractive indexes between 1.37 (ethylacetate) and 1.47 (chloroform). Therefore, the C16-C8FSi-Mag layers are delaminated, forming nanosheets. Two peaks at 1.92° and 2.28° appeared for the cast film of C16-C8FSi-Mag as shown in Fig. 2(C). The peak at lower angle was similar to that observed for the C16 crystals, therefore, a portion of intercalated C16 are deposited on the surface of the sample and the interlayer spacing of C16-C8FSi-Mag slightly decreased to 3.9 nm. After refluxing the C16-C8FSi-Mag film in toluene, the diffraction peak shifted to higher angle of 4.6° and the interlayer spacing decreased to 1.92 nm which was smaller than that of the pristine C8FSi-Mag. This indicates that the weakly bound C16 molecules were removed from the interlayer spacing of Mag, remaining covalently bound C8FSi, though the decrease of interlayer spacing from that of pristine C8FSi-Mag suggests some loss of C8FSi and/or residual C12TMA.

Fig. 3 shows the IR spectra of C16-C8FSi-Mag and C8FSi-Mag thin-film samples. The peaks due to intercalated C16 molecules at 3338, 1658, 1571 ($-NH_2$), 2958, 2924, 2854, 1490 ($-CH_2-$ and CH_3-) and 1245 cm^{-1} (C–N) observed for C16-C8FSi-Mag thin-film completely or almost disappeared after refluxed in toluene. This strongly indicates that the C16 molecules both on the surface and in the layer of C8FSi-Mag were completely removed. On the other hand, in the spectrum of C8FSi-Mag, the absorption peaks at 912 (Si–OH), 1074 (Si–O) and at around 1200 cm^{-1} (perfluoroalkyl groups) were still observed, though the peak due to $-CH_2-$ at 2924 and 2854 cm^{-1} of C8FSi became very weak. These also indicate that the C8FSi-Mag film without C16 was obtained. The intercalated C16 molecules are weakly bonded to silylated Mag by hydrogen bonding with silanol groups and hydrophobic interaction with perfluoroalkyl groups. Therefore, at a high temperature in toluene, C16 molecules are easily removed.

Fig. 4 shows the SEM images of C8FSi-Mag powder, C16-C8FSi-Mag powder, and C8FSi-Mag thin-film, together with the photograph of C8FSi-Mag thin-film on quartz substrate. The obtained C8FSi-Mag thin-film was transparent as shown in Fig. 4(E). The pristine Mag powder possessed the typical "cauliflower" morphology with open aggregation of plates of around 3 μm. These plates appeared to disaggregate slightly when Mag was silylated by C8FSi (Fig. 4(A)). When C16 molecules were intercalated into C8FSi-Mag, the morphology drastically changed. The C16-C8FSi-Mag (Fig. 4(B)) powder consisted of thin plate like particles of mainly around 100 μm, with high aspect ratios. These large plates consist of smaller plates with the size of 1–5 μm. During the intercalation process of C16 molecules into C8FSi-Mag, delamination and reorientation of the layers of C8FSi-Mag occurred, giving the change in morphology. The C16-C8FSi-Mag powder was well dispersed in chloroform and ethylacetate solutions or the mixtures of them, suggesting the delamination of C16-C8FSi-Mag layers. The delaminated layers appear to be densely deposited on the substrate and transparent film with relatively smooth surface was obtained by casting the solution as shown in Fig. 4(C) and (D), though some large particles with the size of around 20 μm were observed. This morphology was quite different from that observed for the turbid film of Mag silylated by [2-(perfluorohexyl)-ethyl]dimethylclhorosilane which was prepared from 2-[perfluorohexyl]ethanol solution [21]. It was composed of oriented aggregates of silylated Mag with their basal plane parallel to the substrate, however, the aggregates are not densely deposited.

Fig. 5 shows the photographs of thin-films of C8FSi-Mag, C16-C8Si-Mag and C8Si-Mag, in comparison with the transparent C16-C8FSi-Mag film (Fig. 5(A)). Partially turbid thin-film was obtained when the dispersion of C8FSi-Mag without C16 molecules was cast on the substrate (Fig. 5(B)). Starting from the dispersion of C8Si-Mag without perfluoroalkyl groups, most part of the thin-film was turbid (Fig. 5(D)). When C16 molecules were added to C8Si-Mag,

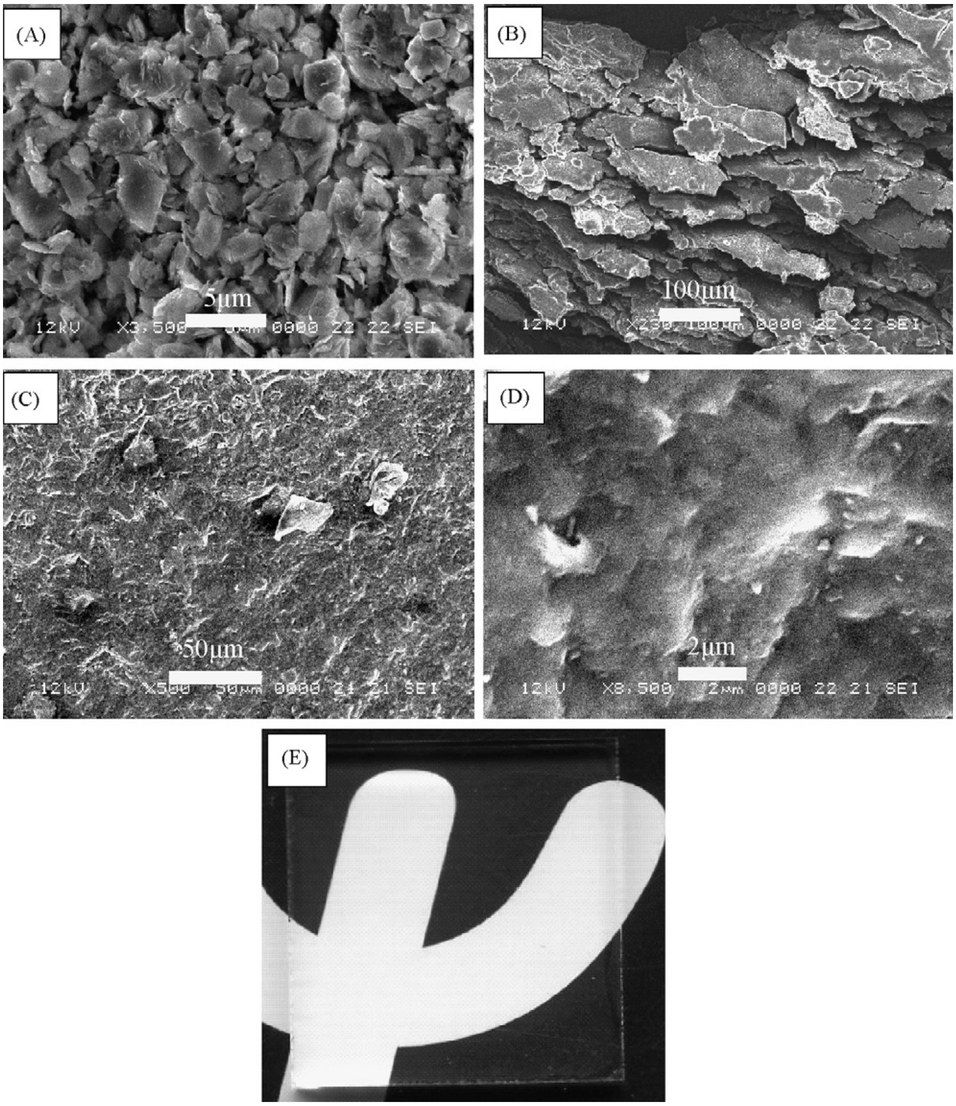


Fig. 4. SEM images of (A) C8FSi-Mag powder, (B) C16-C8FSi-Mag powder and (C), (D) C8FSi-Mag thin-film, together with a (E) photograph of C8FSi-Mag thin-film on quartz substrate.

transparent and translucent regions coexisted, as shown in Fig. 5(C). These results indicate that both C16 molecules and perfluoroalkyl groups are needed to obtain transparent thin-film of silylated magadiite with smooth surface. The effect of the addition of perfluoroalky groups and C16 molecules is not clear at this moment, however, several factors such as heavier and more flat nanosheet of silylated magadiite, lower interaction between perfluoroalkyl groups and/or alky groups would be responsible for the transparent thin-film with smooth surface. The nanosheet of silylated Mag becomes heavier when the silylated Mag contains perfluoroalky groups and C16 molecules. It is expected that the heavier nanosheets readily deposit on the substrate during film formation process before forming larger aggregates in the solution. Lower interaction between perfluoroalky groups also prevents the aggregation of the nanosheets. In case of C16-containing silylated magadiites, the surface of the Mag layers are fully covered with alkyl of perfluoroalkyl groups and the interaction between those bonded to different Mag layers is expected to be very weak, because it is difficult to form interdigitated monolayer structure and the contact area of them becomes smaller. This also prevents the aggregation of the nanosheets. In addition, the size of the perfluoroalkyl groups is larger than that of alkyl ones, therefore, the organic components more fully cover the Mag sheet for C16-C8FSi-Mag. The above effect should be more effective for C16-C8FSi-Mag-containing perfluoroalkyl groups.

2.2. Covalent attachment of pyrene to silylated magadiite thin-film

Fig. 6 shows the X-ray diffraction patterns of C8FSi-Mag reacted with APTES and then with PyBA-S, together with that before reaction. The diffraction peak at $2\theta = 4.56^\circ$ observed for C8FSi-Mag shifted to lower angle of $2\theta = 3.40^\circ$ after reaction with APTES, indicating the silylation of C8FSi-Mag. The interlayer spacing increased from 1.94 to 2.60 nm. Considering the molecular length of C8FSi (1.3 nm) and the thickness of hydrated form of Mag (1.15 nm), the orientation of perfluoroalkyl chains in the layer of Mag changed form monolayer to bilayer type. It was difficult to determine the amount of APTES attached to Mag precisely, however, when powder sample of C8FSi-Mag was silylated by APTES in the same manner, it was about one molecule per Mag unit based on the elemental analysis data of carbon, hydrogen, nitrogen and fluorine, together with the Si content estimated from the TG measurement. The increase of the amount of organic components between the layers of Mag resulted in the increase of interlayer

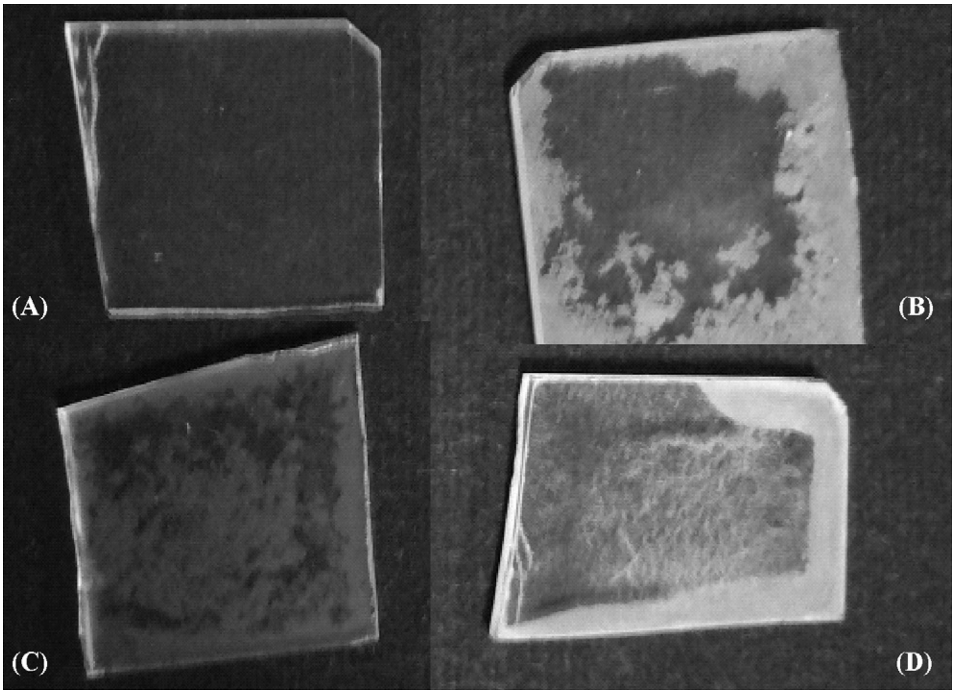


Fig. 5. Photographs of (A) C16-C8FSi-Mag, (B) C8FSi-Mag, (C) C16-C8Si-Mag and (D) C8Si-Mag thin-films on glass substrate.

spacing and the change of the orientation of perfluoroalkyl chains. When APTES-C8FSi-Mag was reacted with PyBA-S, the diffraction peak slightly shifted to lower angle and the interlayer spacing reached 2.74 nm. This indicates that the density of organic component in the layer of APTES-C8FSi-Mag increased most likely due to the introduction of pyrene chromophores and perfluoroalkyl groups took more perpendicular orientation against the layer of Mag. Fig. 7 shows the change of the absorbance at 345 nm of PyBA-S solution (DMF; 2.5×10^{-5} M, 1.8 ml in a quartz cell for UV measurement) in the presence of APTES-C8FSi-Mag thin-film (0.4 mg) on a quartz substrate (0.2 mm × 8 mm × 8 mm). For the reference, quartz substrate reacted with APTES for 1 h in toluene and C8FSi-Mag thin-film without APTES also immersed in PyBA-S solution independently. The absorption decreased in all cases, suggesting that PyBA-S molecules are physically adsorbed onto C8FSi-Mag and are attached to the quartz substrate reacted with APTES. The decrease of the absorbance was apparently larger when APTES-C8FSi-Mag thin-film was immersed. From the change of the absorbance during reaction for 2 h, the pyrene chromophore introduced into the APTES-C8FSi-Mag was roughly estimated by subtracting physically adsorbed PyBA-S and covalently attached PyBA-S to quartz substrate treated by APTES, and the value of 0.007 pyrene chromophore per Mag unit of $Si_{14}O_{29}$ was obtained.

Fig. 8 shows the IR spectra of the above samples. Together with the strong absorption peak due to Si–O vibration at 1074 cm^{-1}, the peaks around 1200 and 897 cm^{-1} derived of perfluoroalkyl and Si–OH groups, respectively, were observed for the pristine C8FSi-Mag. The Si–OH groups are originated from the hydrolysis of Si–Cl groups of silylating reagent which were not used for the formation of Si–O bonding during silylation of Mag. After reaction with APTES, the absorption peak at 897 cm^{-1} almost disappeared, which means that silylation of C8FSi-Mag occurred as was observed for the reaction between silylated graphite oxide and pyrene-containing triethoxysilane [8]. The absorption peak due to Si–O vibration slightly shifted to 1078 cm^{-1} at the same time. The increase of absorption around 2900 cm^{-1} due to –CH_2– groups also

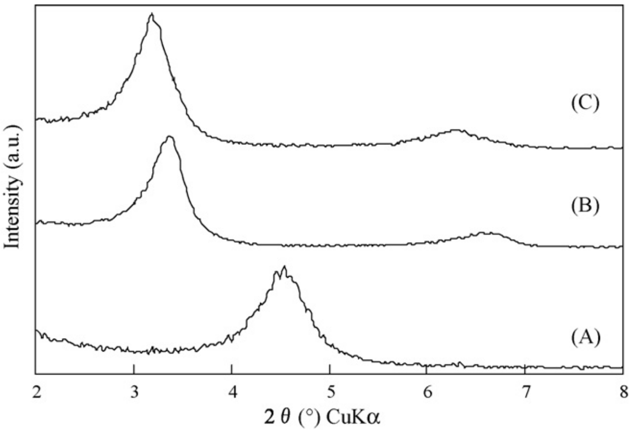


Fig. 6. X-ray diffraction patterns of (A) C8FSi-Mag, (B) APTES-C8FSi-Mag and (C) PyBA-APTES-C8FSi-Mag thin-films.

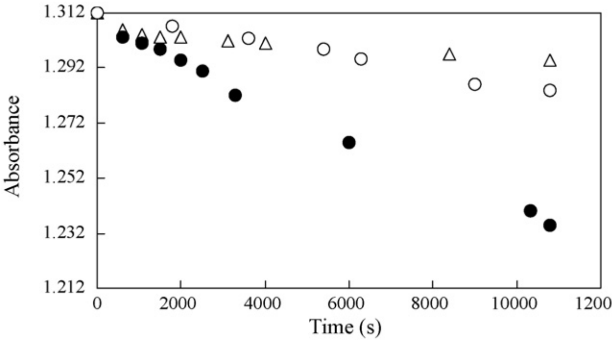


Fig. 7. The change of absorbance at 345 nm of PyBA-S in DMF (2.5×10^{-5} M, 1.8 ml) during reaction with APTES-C8FSi-Mag thin-film (filled circles), C8FSi-Mag thin-film (open circles) and quartz substrate reacted with APTES (open triangles).

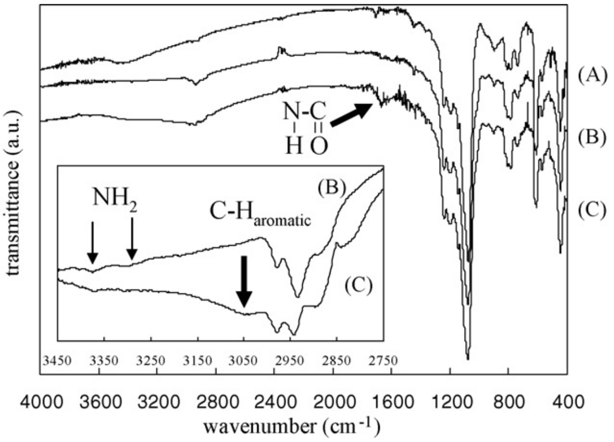


Fig. 8. IR spectra of (A) C8FSi-Mag, (B) APTES-C8FSi-Mag and (C) PyBA-APTES-C8FSi-Mag thin-films. Inset: expanded spectra of (B) and (C).

indicated the introduction of APTES into C8FSi-Mag, though the absorption peak from amino groups was not apparently observed around 1600 cm^{-1}. When APTES-C8FSi-Mag was immersed in the solution of PyBA-S, absorption peak at 1680 cm^{-1} due to carboxyl groups appeared as shown the inset of Fig. 8. This suggests that the amino groups introduced between the layers of C8FSi-Mag were successfully reacted with PyBA-S, forming amide groups.

Fig. 9 shows the UV–vis and fluorescence spectra of PyBA-APTES-C8FSi-Mag thin-film. The spectral shapes were very similar to those of PyBA-S in DMF solution and the absorption peaks were observed at 2–3 nm shorter wavelengths. These shifts of absorption peak could be ascribed too less polar environment of pyrene moiety surrounded by perfluoroalky groups in silylated Mag. The fluorescence peaks were observed at almost the same positions as those of PyBA-S in DMF solution and no peak due to pyrene excimer around 460 nm was observed, indicating that the pyrene chromophores are well separated with each other. Similar fluorescence spectrum was observed when C8FSi-Mag thin-film without amino groups was treated in the same way, however, the fluorescence and absorption peaks almost disappeared when the resulting film was immersed in acetone. This indicates that the PyBA-S molecules were also introduced into the C8FSi-Mag film, however, they were bonded to it by weaker hydrophobic interaction and were readily removed during immersion in acetone. On the other hand, no spectral change was observed for the film prepared from APTES-C8FSi-Mag. This also shows that the introduced PyBA-S molecules are strongly bonded to the layers of APTES-C8FSi-Mag.

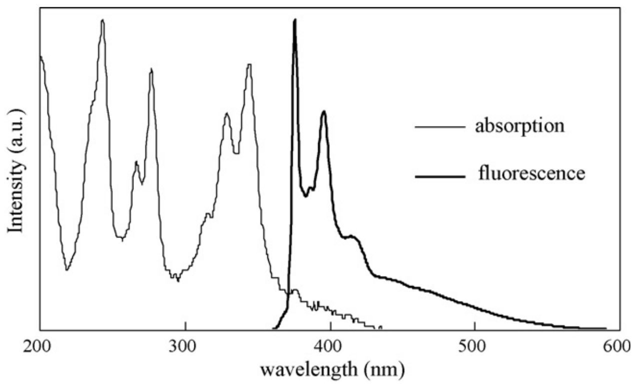


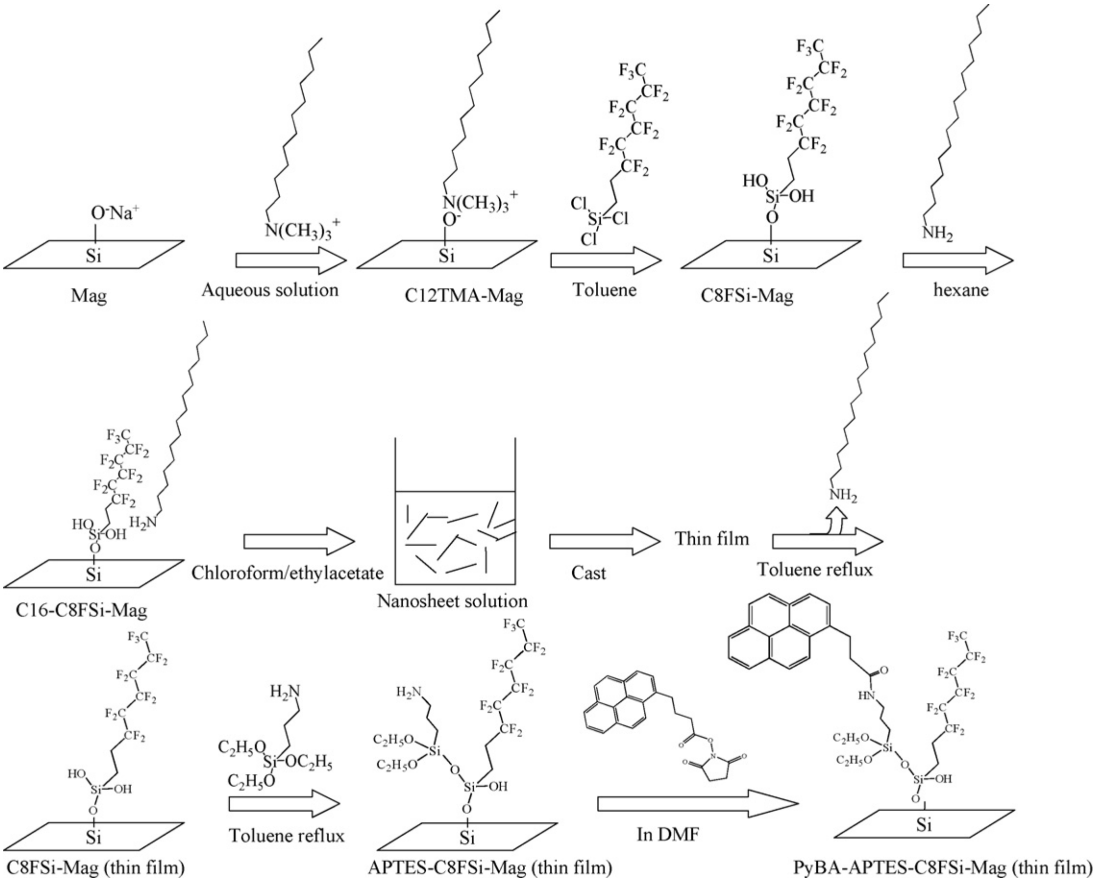
Fig. 9. Absorption (A) and fluorescence (B) spectra of PyBA-APTES-C8FSi-Mag thin-film.

3. Conclusion

Transparent thin-film of silylated magadiite-containing perfluoroalkyl groups was successfully prepared by casting the nanosheet solution of it. The perfluoroalkyl groups and *n*-hexadecylamine in silylated magadiite made the nanosheet of it heavier and more flat, resulting in the smoother surface of the thin-film of silylated magadiite. The amino groups were attached to the silylated magadiite thin-film-containing perfluoroalkyl groups and then 1-pyrenebutanoic acid succimidyl ester was reacted with it. Pyrene chromophores were covalently attached to the layer of silylated magadiite. The present method to prepare thin-film sample of silylated magadiite and to attach dye molecules to it would be very useful to obtain various photo-functional silylated magadiite.

4. Experimental

Magadiite (abbreviated as Mag) was prepared and silylated, according to the literatures [17,18]. The mixture of amorphous silica, NaOH and water with the molar ratio of 1:0.23:18.5 was sealed in a Teflon-lined autoclave and treated hydrothermally at 150 °C for 2 days. The resulting solid product was washed with dilute NaOH aqueous solution and dried at 60 °C. Dodecyltrimethylammonium-Mag (abbreviated as C12TMA-Mag) was prepared by mixing Mag (3 g) and aqueous solution of dodecyltrimethylammonium chloride (0.1 M, 200 ml). The resulting precipitate was filtered off. The C12TMA-Mag (150 mg) was silylated by [2-(perfluorohexyl)-ethyl]trichlorosilane ($C_8F_{13}H_4SiCl_3$, hereafter C8FSi; 1 ml) in toluene (10 ml) at 60 °C for 2 days. The silylated product was filtered off and washed with acetone several times and dried at 60 °C. The thermogravimetric analysis indicated that the composition of the silylated Mag (abbreviated as C8FSi-Mag) was approximately $(C8FSi)_{2.3}Si_{14}O_{29}$, in which slightly higher amount of perfluoroalkyl chains was contained as that reported for Mag silylated by [2-(perfluorohexyl)-ethyl]dimethylchlorosilane [21]. For comparison, Mag was silylated by octyltrichlorosilane ($C_8H_{17}SiCl_3$, hereafter C8Si; 1 ml) and $(C8Si)_{2.1}Si_{14}O_{29}$ was obtained. Intercalation of hexadecylamine (abbreviated as C16) was performed in the same way as reported in the literature [26,27]. The mixture of silylated Mag samples and C16 with the weight ratio of C8FSi-Mag/C16 = 1 was ground in a pestle in the presence of hexane (ca. 0.2 ml) until it was evaporated and the resulting powder was dried at 60 °C overnight. The obtained sample (denoted as C16-C8FSi-Mag) was dispersed in the mixture of chloroform and ethylacetate (2 mg/ml, 1:1, v/v) and sonicated for 15 min. Thin-films of C8FSi-Mag samples were prepared by casting this solution (0.05 ml/cm^2) on quartz, glass or silicon substrates. The C16 molecules were then removed from the sample by immersing it in toluene under reflux for 1 h. This film was refluxed in the toluene solution of 3-aminopropylethoxysilane (abbreviated as APTES, 0.1 M, 15 ml) for 1 h in order to introduce amino groups. After reaction, the sample (denoted as APTES-C8FSi-Mag) was washed with acetone several times. Introduction of pyrene chromophore into C8FSi-Mag was performed by immersing it in the *N*,*N*-dimethylforamide (DMF) solution of 1-pyrenebutanoic acid succinimidyl ester (abbreviated as PyBA-S, 2.5×10^{-4} M, 5 ml) shown Fig. 1 at 60 °C for 1 day. The products were washed with acetone several times. These procedures are schematically illustrated in Scheme 1. The samples were analyzed by X-ray diffractometry (Rigaku Rint-2100, Cu Kα radiation), UV–vis absorption (Hitachi U-2000) and fluorescence spectroscopy (Hitachi F-3100 excitation wavelength of 330 nm). The FT-IR data was collected using Nicolet Avatar 360 spectrometer for thin-film samples prepared on silicon substrate. SEM observation was conducted by using JEOL-5600 and Pt was sputtered onto the samples before observation.



Scheme 1. The procedure used for the sample preparation.

Acknowledgement

This work was financially supported by the Grant-in-Aid for Scientific Research (C) (No. 19550196) from Ministry of education, culture, sports and science, Japan.

References

[1] V. Ramamurthy, J. Photochem. Photobiol. C 1 (2000) 145.
[2] M. Ogawa, K. Kuroda, Bull. Chem. Soc. Jpn. 70 (1997) 2593.
[3] M. Ogawa, J. Photochem. Photobiol. C 3 (2002) 129.
[4] T. Shichi, K. Takagi, J. Photochem. Photobiol. C 1 (2002) 113.
[5] G. Shulz-Ekloff, D. Wöhrle, B. Van Duffel, R.A. Schoonheydt, Microporous Mesoporous Mater. 51 (2002) 91.
[6] Y. Matsuo, T. Fukutsuka, Y. Sugie, Chem. Lett. 32 (2003) 1004.
[7] Y. Matsuo, N. Yamada, T. Fukutsuka, Y. Sugie, Mol. Cryst. Liquid Cryst. 452 (2006) 133.
[8] Y. Matsuo, T. Fukutsuka, Y. Sugie, Chem. Lett. 35 (2006) 530.
[9] H.P. Eugster, Science 157 (1967) 1177.
[10] G. Lagaly, K. Beneke, A. Weiss, Am. Miner. 60 (1975) 642.
[11] G. Lagaly, K. Beneke, A. Weiss, Am. Miner. 60 (1975) 650.
[12] J.M. Rojo, E. Ruiz-Hitzky, J. Sanz, Inorg. Chem. 27 (1988) 2785.
[13] E. Ruiz-Hitzky, J.M. Rojo, Nature 287 (1980) 28.
[14] E. Ruiz-Hitzky, G. Lagaly, J.M. Rojo, Colloid Polym. Sci. 263 (1985) 1025.
[15] T. Yanagisawa, K. Kuroda, C. Kato, React. Solids 5 (1988) 167.
[16] T. Yanagisawa, K. Kuroda, C. Kato, Bull. Chem. Soc. Jpn. 61 (1988) 3743.
[17] K. Kosuge, A. Yamazaki, A. Tsunashima, R. Otsuka, J. Ceram. Soc. Jpn. 100 (1992) 326.
[18] S. Okumoto, K. Kuroda, M. Ogawa, Appl. Clay Sci. 15 (1999) 253.
[19] M. Ogawa, S. Okumoto, K. Kuroda, J. Am. Chem. Soc. 120 (1998) 7361.
[20] I. Fujita, K. Kuroda, M. Ogawa, Chem. Mater. 17 (2005) 3717.
[21] M. Ogawa, M. Miyoshi, K. Kuroda, Chem. Mater. 10 (1998) 3787.
[22] M. Brinkley, Bioconjugate Chem. 3 (1992) 2.
[23] S. Huber, G. Calzaferri, Angew Chem. Int. Ed. 43 (2004) 6738.
[24] M. Ogawa, Y. Ide, J. Colloid Interf. Sci. 296 (2006) 141.
[25] T. Nakato, S. Hashimoto, Chem. Lett. 36 (2007) 1240.
[26] Y. Matsuo, K. Watanabe, T. Fukutsuka, Y. Sugie, Carbon 41 (2003) 1545.
[27] Y. Matsuo, T. Fukunaga, T. Fukutsuka, Y. Sugie, Chem. Lett. 33 (2004) 1432.