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Review

Synthesis, structure and properties of intercalation compounds containing perfluoroalkyl groups

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Abstract

Synthesis, structure and properties of various layered materials containing perfluoroalkyl groups in their interlayer space were summarized. They were obtained by ion exchange method for layered materials with ion exchange capacity and by silylation technique for those possessing acidic hydroxyl groups. The orientation of perfluoroalkyl groups greatly changed depending on their contents in the layered materials. The nature of the interlayer space of them changed from hydrophilic to hydrophobic and they were well dispersed in appropriate organic solvents. Some of them formed so called nanosheet solution and film samples were prepared from it. Organic molecules were introduced into the intercalation compounds by co-adsorption or exfoliation–restacking methods. The empty space surrounded by perfluoroalky chains where organic molecules are included showed unique properties. The weak interaction between perfluoroalkyl chains and included organic molecules lead the easy diffusion of them in the interlayer space, which caused the aggregation of them or affected the distribution of isomers obtained by photochemical reaction. The low vibrational C–F bonding in perfluoroalky groups reduced radiational quenching, accordingly enhanced the fluorescence from included organic dyes.

Keywords: Layered materials; Intercalation; Perfluoroalkyl groups; Ion exchange; Silylation; Photophysical properties; Photochemical reactions

Contents

1. Introduction

Perfluoroalkyl groups are known to show various interesting properties such as thermal, adhesive, frictional, electrical and photophysical properties which are mainly originate from the high electronegativity of fluorine atom and low polarizability of C–F bonding [1]. Concerning the photophysical properties, materials containing perfluoroalkyl chains are highly transparent and possess low refractive index [2,3]. Therefore, these materials are used as optical fibers, coating of display, matrices of dyes, etc. The perfluoroalkyl environment is also interesting from the view point of microenvironment for chemical

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reactions because of weak solvent–solute interaction, accordingly relatively higher solute–solute interaction [4,5].

On the other hand, layered materials with two-dimensional structure are useful for the matrices of photofunctional molecules [6,7]. When the organic molecules are included in the two dimensional space of layered materials, it is expected to form ordered structure, which is favorable for the optical applications. Therefore, when perfluoroalkyl groups are combined with layered materials, it is expected to observe various interesting phenomena.

In this paper, therefore, recent studies on the synthesis and properties of intercalation compounds containing perfluoroalkyl groups are reviewed.

2. Preparation of intercalation compounds containing perfluoroalkyl groups

Three types of synthetic methods are known in order to introduce perfluoroalkyl groups into layered materials, including ion exchange reaction using ions containing perfluoroalkyl groups, silylation by silylating reagents with perfluoroalkyl chains and oxidative intercalation of anions possessing them. The last one has been used for the introduction of them into graphite and this is summarized elsewhere [8].

Layered materials such as clay minerals possess ion exchange capability and the ions in the interlayer spacing can be exchanged by foreign ions simply immersing in an appropriate solution containing them [9]. The exchangeable ions in clay minerals are usually cation; therefore, the amount of them per gram is called cation exchange capacity (CEC). The degree of ion exchange can be controlled by the concentration of cations.

The second one is the silylation of layered materials using silylating reagents containing perfluoroalkyl groups such as perfluoroalkylchlorosilanes in organic solvents [10–12]. The acidic hydroxyl groups on the layer of layered materials can react with them and perfluoroalkyl groups are introduced via Si–O bonding by releasing hydrogen chloride.

The layered materials, which have been used as the hosts of perfluoroalkyl groups, are summarized in Table 1. The other layered materials possessing ion exchange capability or acidic hydroxyl groups would be also expected to react with the reagents containing perfluoroalkyl groups in a similar manner.

2.1. Preparation of intercalation compounds containing perfluoroalkyl groups by ion exchange method

Inoue et al. have reported the intercalation of cationic polyfluorinated surfactants with different perfluoroalkyl chain lengths ($C_nF_{2n+1}CONH(CH_2)_2N^+(CH_3)_2(C_{16}H_{33})Br^-$; $n = 1$–3, abbreviated as C*n*F–S) into saponite clay [13]. The interesting observation in this system was the intercalation of C3F–S with the longest perfluoroalkyl chain length largely exceeding the CEC of saponite (0.997 mequiv./g). This is ascribed to the co-adsorption of surfactant cation together with the counter anion of Br^-. The maximum limit of the intercalation is believed to depend on the microscopic structure around the ammonium head group of the surfactant. The C3F–S molecules which showed the largest intercalation up to 4.4 times of CEC possesses the smallest occupied area as shown later. The schematic structure of C3F–S/saponite hybrid based on the X-ray diffraction data is summarized in Fig. 1. At low ion exchange level, the surfactant molecules can induce the formation of ordered structure. When the exchange level reached 1.0 CEC, the surfactant molecules form bilayer structure as shown in Fig. 1(b). At the loading levels greater than 1.7 times of CEC, the excess intercalation proceeds by an incorporation of surfactant as a neutral molecule via hydrophobic interaction, forming densely packed structure.

Graphite oxide (abbreviated as GO), which was prepared by oxidizing graphite in concentrated oxo-acids, was also used as a host material. Graphite oxide possesses a large amount of acid hydroxyl groups on its layer [14] and simply by mixing with excess [(2-perfluorohexyl)-ethyl]amine (hereafter, FHEN) in the presence of a small amount of hexane, intercalation readily occurred. This method is not ion exchange, however, the hydroxyl groups possessing ion exchange ability in GO is believed to be responsible for the intercalation of it and, neutral and ammonium type amines coexist in the layer of GO [15]. Just after evaporation of hexane, the amine content was 0.62 mol/GO unit and it gradually decreased to 0.38 mol/GO unit as the intercalation compound was left in the ambient atmosphere [16]. This final amine content in GO was much smaller than that of octylamine-intercalated GO (amine/GO ratio of 1.55) [15]. It has been suggested that the alkylamine content in GO increase with the increase of the carbon numbers in them because the hydrophobic interaction between them became

Table 1
Composition and interlayer spacings of intercalation compounds containing perfluoroalkyl groups

Host	Intercalated species	Method	Composition
Saponite (abbreviated as SA): $[(Si_{7.20}Al_{0.80})(Mg_{5.97}\mathrm{A1}_{0.03})O_{20}(OH)_4]^{-0.77}(Na_{0.49}Mg_{0.14})^{+0.77}$	$C_nF_{2n+1}CONH(CH_2)_2N^+(CH_3)_2(C_{16}H_{33})Br^-$ (abbreviated as C*n*F–S (n = l–3))	Ion exchange	<4.4 CEC[a]
Magadiite $Na_2Si_{14}O_{29}$ $2H_2O$	$CF_3(CF_2)_5(CH_2)_2Si(CH_3)_2Cl$ (abbreviated as FHESCl)	Silylation	$[(FHES)_{1.6}H_{0.4}]Si_{14}O_{29}$
Graphite oxide $C_8O_{4.0}H_{3.0}$[b] (abbreviated as GO)	$CF_3(CF_2)_5(CH_2)_2NH_2$ (abbreviated as FHEN)	Direct intercalation	$(FHEN)_{0.38\text{–}0.62}GO$
	$CF_3(CF_2)_7(CH_2)_2SiCl_3$ (abbreviated as $FOESCl_3$)	Silylation	$(FOESOH)_{0.45}GO(C_4H_9NH_2)_{0.40}$

[a] CEC: cation exchange capacity; 0.997 meq/g.

[b] The composition of graphite oxide greatly varies depending synthetic methods and ambient humidify.

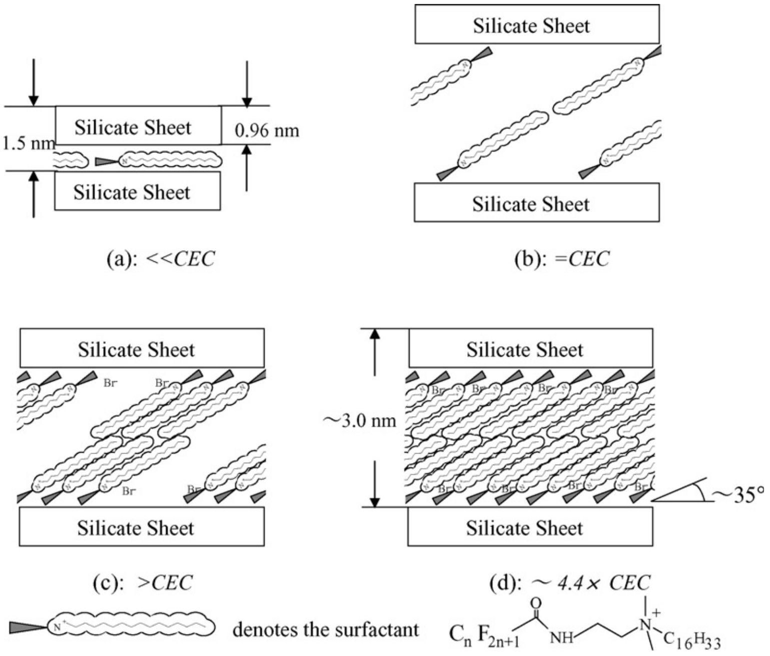

Fig. 1. Schematic structure of C3F–S/saponite clay hybrid compound for various amounts of adsorbed C3F–S molecules: (a) very small amounts vs. CEC, (b) equal to CEC, (c) amounts in excess of CEC, and (d) 4.4 times CEC. From Ref. [13].

larger. The weaker interaction between FHEN molecules resulted in the lower amine content in GO. At the beginning of the reaction, the perfluoroalkyl chains in $(FHEN)_{0.62}GO$ oriented almost perpendicularly against GO layer, however, when the excess amine was removed, they took interdigitated monolayer orientation with tilted perfluoroalkyl chains as shown in Fig. 2.

2.2. Recovery of perfluorinated surfactants using layered materials by ion exchange

By using ion exchange technique, recovery of perfluorinated surfactants such as perfluorooctane sulfonate and perfluorooctanic acid is conducted [17]. Layered double hydroxides (LDH) [18] with anion exchange capacity are considered for recovery of them. When Zn/Al–LDH is immersed in the aqueous solutions of the above surfactants, more than 90% of them were removed from the solution as shown in Table 2. Fig. 3 shows the X-ray diffraction pattern of the Zn/Al–LDH after adsorption of perfluorooctanic acid. The interlayer spacing reached 2.9 nm, suggesting the CO_3^{2-} ions in Zn/Al–LDH were exchanged by perfluorooctanic acid and the intercalated surfactants are oriented almost perpendicularly to the layer with bilayer structure.

2.3. Introduction of perfluoroalkyl groups into layered materials by silylation

The hydroxyl groups in layered materials such as silicates including magadiite, octosilicate, kenyaite and kanemite, and graphite oxide react with silylating reagents such as alkylchlorosilanes or alkylalkoxysilanes [9–12]. As exfoliating reagents, alkyltrimethlyammonium ion or alkylamine was introduced into the layer and then the resulting material was

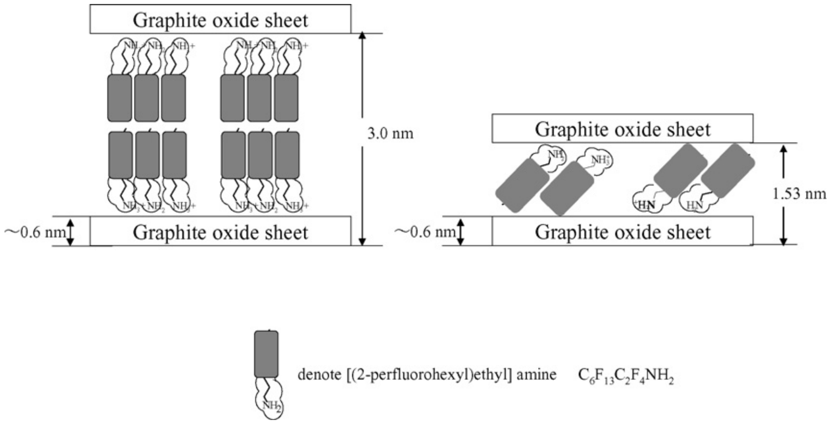

Fig. 2. Schematic structure of FHEN-intercalated graphite oxide. Left: higher FHEN content; right: lower FHEN content.

Table 2
Removal of perfluorooctanoic acid and perfluorooctane sulfonate from aqueous solution

Surfactant	Initial concentration (wt%)	Final concentration (ppm)	Removed surfactant (%)
Perfluorooctanoic acid	0.01	9	91.0
	0.1	13	98.7
	1	78	99.2
	10	93	99.9
Perfluorooctane sulfonate	0.01	12	88.0
	0.1	14	98.6
	1	51	99.5

dispersed in organic solvents, which facilitates the access of silylating reagents to the interlayer spacing of layered materials. Hydroxyl groups react with silylating reagents forming Si–O covalent bonding and exfoliating reagents are excluded from the layer. The formation of Si–O bonding is accompanied by the release of hydrogen chloride, which is usually harmful for the resulting material and they are trapped by base such as pyridine.

Fig. 4 shows the X-ray diffraction patterns of magadiite during silylation of it [19]. The interlayer spacing of sodium–magadiite was 1.56 nm and it increased to 2.81 nm after exchange reaction by dodecyltrimethylanmonium cations (hereafter abbreviated as $C_{12}TMA$). When the resulting sample was silylated by [2-(perfluorohexyl)-ethyl]dimethylchlorosilane (hereafter abbreviated as FHES), the diffraction peak slightly shifted to lower angle, indicating the increase of interlayer spacing. The composition of FHES–magadiite determined from the elemental analysis was $[(FHES)_{1.6}H_{0.4}]$-$Si_{14}O_{29}$. The ^{29}Si NMR spectrum showed that a signal due to the M^1 environment of silicon ($Si–O–\mathit{Si}–R_3$) appeared at 22.8 ppm. These indicated that perfluoroalkyl groups were successfully introduced into the layer of magadiite. The important characteristic of this compound was a film-forming capability. It was dispersed in 2-(perfluorohexyl)ethanol with sonication and turbid thin film was obtained by casting the supernatant solution [19].

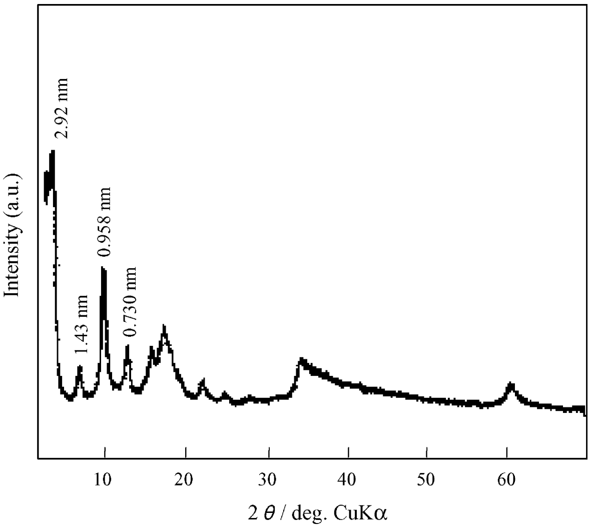

Fig. 3. X-ray diffraction pattern of Zn/Al–LDH immersed in aqueous solution of perfluorooctanoic acid. From Ref. [17].

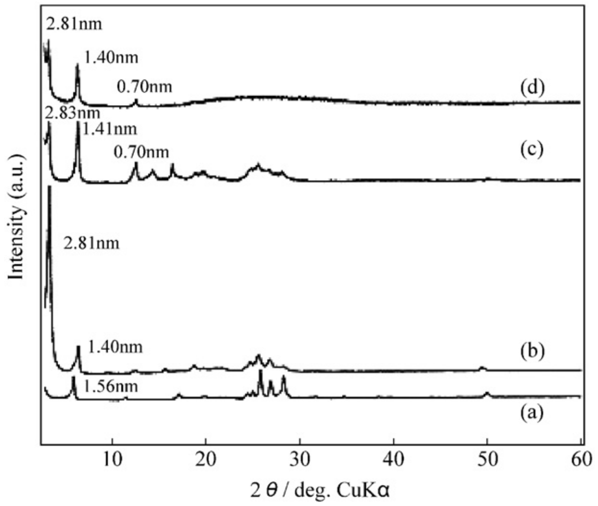

Fig. 4. X-ray diffraction patterns of (a) Na-magadiite, (b) the C12TMA-magadiite, (c) the FHES–magadiite, and (d) the cast films of the FHES–magadiite. From Ref. [19].

GO similarly reacts with silylating reagents containing perfluoroalkyl groups [20]. In this case, in order to facilitate the exfoliation of graphite oxide layers and access of silylating reagents to them, alkylamines were added before reaction [21,22]. Most of the acidic hydroxyl groups of graphite oxide were reacted with silylating reagents and the composition of the resulting material was $(C_6F_{13}C_2H_4OH)_{0.45}GO(C_4H_9NH_2)_{0.38}$. Considerable amount of butylamine used as an exfoliating reagent remained in the sample.

The intercalation compounds and their compositions are summarized in Table 1.

3. Photophysical and photochemical properties of organic molecules in layered materials containing perfluoroalkyl groups

Various organic molecules including organic dyes are introduced into the polyfluorinated environment by co-intercalation or exfoliation–restacking process. Cationic dyes can be easily co-intercalated into polyfluorinated environment by simple ion exchange method. On the other hand, neutral molecules are introduced into the polyfluorinated environment by hydrophobic interaction, using exfoliation–restacking process. The layered materials containing amphiphilic molecules such as surfactants are hydrophobic and soluble in appropriate organic solvents, forming so called nanosheet solution in which they are believed to be exfoliated into individual sheets. When dye molecules are added to this solution, thin film samples containing them are obtained by casting or spin coating of the resulting solution onto appropriate substrates.

Table 3
The absorption and fluorescence maxima of unaggregated RB and estimated dielectric constants in various surfactant clay hybrids

	$\lambda_{A,max}$ (nm)	$\lambda_{F,max}$ (nm)	ε	
			From $\lambda_{A,max}$	From $\lambda_{A,max}$
RB (aq)	549	570		
C1F–S	571	591	9	6
C2F–S	568	588	12	8
C3F–S	563	581	18	18
C1H–S	565	581	16	18
C2H–S	565	581	16	18
C3H–S	565	581	15	16

Estimated from calibration relationship of λ_{max} and solvent polarity. Excitation wavelength = 520 nm. RB in aqueous solution.

3.1. Micropolarity of polyfluorinated environment

One of the most fundamental characteristics of the microenvironments is the micropolarity experienced by the molecules situated in the microcavity in intercalation compounds available for organic molecules [23]. Rose Bengal (abbreviated as RB) is one of the well-known molecules, which are sensitive to the polarity of the solvent and this was used to estimate the micropolarity in the C*n*F–S-intercalated saponite as a probe molecule. Table 3 shows the absorption and fluorescence maxima of unaggregated RB and estimated dielectric constants in surfactant/clay hybrids. The absorption and fluorescence maxima of RB molecules in the microcavitiy surrounded by perfluoroalky groups were both observed at longer wavelength that those in water, meaning that they are situated in less polar environment. However, surprisingly, it shifted to blue as the increase of perfluoroalkyl chain length, while this phenomenon was not observed in the system without perfluoroalky groups. Based on the adsorption behavior of water onto the above intercalation compounds, the more polar environment in the intercalation compound with longer perfluoroalkyl chains was explained by the higher water content in the vicinity of ammonium groups where RB molecules are situated as shown in Fig. 5. The high water content for the sample with longer perfluoroalkyl chains was confirmed by the water adsorption measurement by using quartz microbalance. The water content increased with the increase of C3F–S loading, when the sample possessed ordered structure as shown in Fig. 1. Water molecules are considered to prefer the aligned ammonium groups as good adsorbing sites.

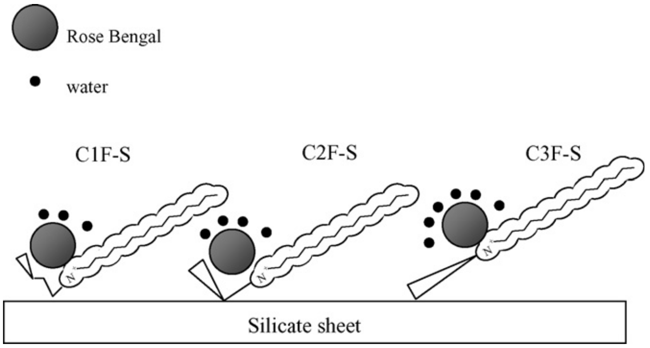

Fig. 5. Schematic orientational structure of RB and polyfluorinated surfactants in a clay hybrid layer and corresponding occupied area of each polyfluorinated surfactant. From Ref. [13].

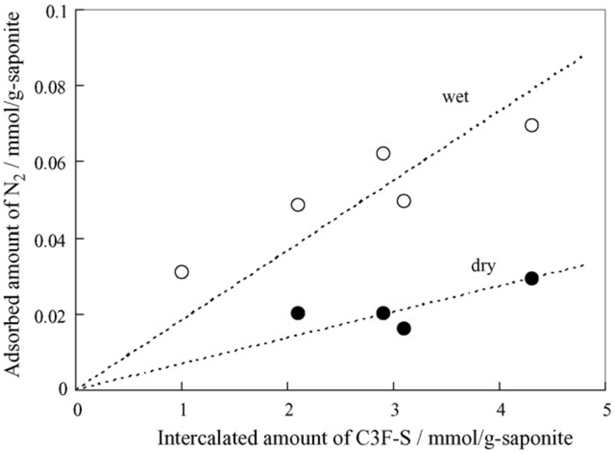

Fig. 6. Effect of the intercalated amount of C3F–S on nitrogen adsorption. The wet sample contains pre-adsorbed water (0.3 mmol/g saponite). From Ref. [24].

The other interesting phenomenon observed for C3F–S-intercalated saponite was the enhanced adsorption of gaseous molecules onto intercalation compounds containing pre-adsorbed water [24]. Fig. 6 shows the adsorbed amounts of nitrogen gas as a function of intercalated amount of C3F–S. They were apparently higher than those observed in the absence of pre-adsorbed water and increased almost linearly. Since the size of the microcavity becomes smaller, it is not the site for accommodating gaseous molecules. These indicate that the more specific site directly correlated to the surfactants themselves should exist. This enhanced adsorption was commonly observed for hydrogen, deuterohydrogen, oxygen and ethylene.

3.2. Control of the aggregation of organic dyes in polyfluorinated environment

When polyfluorinated surfactant (C*n*F–S) aqueous solution and organic dyes (tetra(4-sulfonatophenyl)porphyrinatoantimony (V) (Sb(V)TSPP), tetra(4-sulfonatophenyl)-porphyrinatogelmanium (IV) (Ge(IV)TSPP) and tetra(4-sulfonatophenyl)porphyrinatotin (IV) (Sn(IV)TSPP)) were added to the clay dispersion. Co-intercalation of dyes together with polyfluorinated surfactants was achieved [25,26]. The loading level of Sb(V)TSPP was 0.05–0.2% versus CEC. In the intercalation compounds dispersed in aqueous solution, the Sb(V)TSPP molecules were in a monomeric state judging from the Soret maximum (419 nm). This peak shifted to 422 nm upon drying, which indicated that Sb(V)TSPP are in less polar environment.

The intercalation compounds considerably (by 0.8 nm) swell in benzene solution maintaining the layered structure. Fig. 7 shows the absorption spectral change of Sb(V)TSPP during benzene dispersion. During first 60 min of dispersion, the Soret band exhibits a monomer-like absorbance at 422 nm. However, during subsequent 1.5 h, the 422 nm

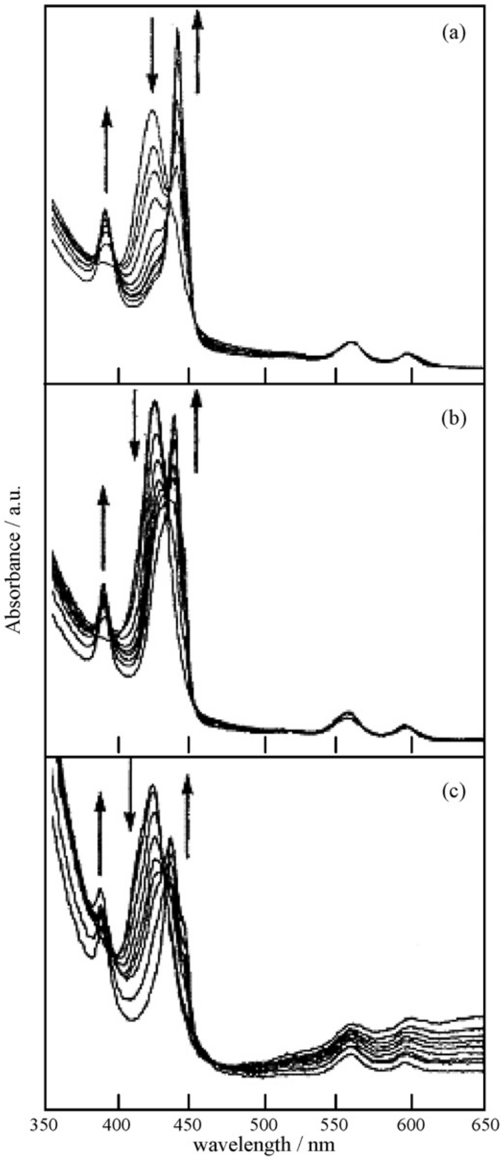

Fig. 7. Absorption spectral changes of Sb(V)TSPP co-intercalated in the polyfluorinated surfactant/clay hybrid compound upon benzene dispersion: (a) C3F–S/Sb(V)TSPP = 270:0.12% CEC, (b) C2F–S/Sb(V)TSPP = 160:0.12% CEC and (c) C1F–S/Sb(V)TSPP = 170:0.12% CEC hybrid compound. From Ref. [26].

monomer band diminished and new bands at 388 and 438 nm. Fluorescence and excitation spectra indicated that these bands are due to H- and J-types dimers, respectively. Here, the H-type dimer includes a stacked orientation of the two porphyrin rings and J-type dimer is described as two porphyrin rings oriented in a staggered structure. On the other hand, surprisingly, the monomer absorption of Sb(V)TSPP at 419 nm remained unchanged after 100 h of benzene dispersion in the surfactant/clay hybrid without perfluoroalkyl groups. The strong lipophobic character of perfluoroalkyl groups may expel the surrounding hydrophobic Sb(V)TSPP molecules, to promote the aggregation under the assistance of benzene in their migration. From the spectral change as a function of time, the kinetics of the above two types of dimer formation were also analyzed and it found that both dimers are formed in a constant ratio from the monomer. The aggregation of Sn(IV)TSPP was commonly observed, however, interestingly, no dimer formation occurred for Ge(IV)TSPP which is deeply trapped in the surfactant assemblies in the layer of clay [25].

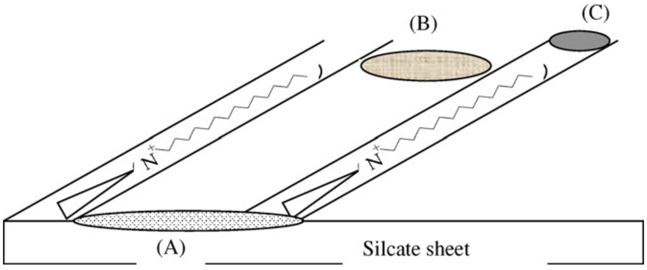

Fig. 8. Schematic drawing if proposed surfactant/clay hybrid microstructure and relationship between the definitions of the following three areas: (A) occupied area, (B) excess area and (C) cross sectional area of alkyl chains (0.26 nm^2). From Ref. [26].

The effect of surfactant concentration was also discussed using the ‘‘occupied areas’’ and ‘‘excess areas’’ as shown in Fig. 8. The occupied areas (1.25 nm^2/anionic site; area A in Fig. 8) is defined as the value of the surfactant area of the clay divided by the value of mole fraction of the adsorbed amount of surfactant versus CEC [23]. The ‘‘excess area’’ (area B in Fig. 8) is defined as the value obtained by subtraction of the cross sectional area of most rigidly packed alkyl chain of an ammonium type surfactant (0.26 nm^2; area C in Fig. 8) from the observed occupied area of each surfactant [23]. Table 4 shows the relation between the adsorbed amount of surfactant and aggregate formation for Sb(V)TSPP in the interlayer space of various intercalation compounds. Aggregation of Sb(V)TSPP was observed only for hybrid containing lower amounts of polyfluorinated surfactant. The polyfluorinated alky groups easily expel the Sb(V)TSPP molecules and this effect is more apparent when the ‘‘excess area’’ for the inclusion of them is larger [26].

These indicate that polyfluorinated microcavity provides a very unique microenvironment that minimized the solute–surrounding environment interaction and to relatively strengthen the intermolecular interaction between solute molecules trapped in the microcavity.

Table 4
Relation between the adsorbed amount of surfactant and aggregate formation for Sb(V)TSPP in the interlayer space of various intercalation compounds

Surfactant	Adsorbed amount of surfactant (% CEC)	Occupied area (nm^2)	Excess area (nm^2)	Aggregate formation
C1F-S	330	0.38	0.12	No
	270	0.46	0.20	Yes
	170	0.74	0.48	Yes (very fast)
C2F-S	250	0.50	0.24	No
	160	0.78	0.52	Yes
C1F-S	170	0.74	0.48	Yes
C3H-S	170	0.74	0.48	No
CTAB	170	0.74	0.48	No

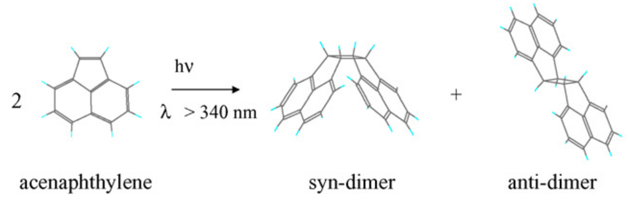

Fig. 9. Photochemical dimerization of acenaphthylene.

3.3. Control of photochemical dimerization of acenaphthylene in polyfluorinated environment

The photochemical dimerization behavior of acenaphthylene included in perfluoroalkylamine-intercalated graphite oxide has been investigated in comparison with that in intercalation compounds without perfluoroalkyl groups. Upon UV irradiation (high pressure UV lamp, $\lambda > 340$ nm), two types of dimers of acenaphthylene as shown in Fig. 9 formed in the film of intercalation compound. It has been reported that more than 95% and about 50% of acenaphthylene molecules in the singlet and triplet excited states, respectively provide *syn*-isomer [27,28]. As the result, *syn*/*anti* ratios of the dimers are more than 19 and about 1, when they are exclusively formed from the singlet and triplet excited states, respectively. The formed dimers were extracted from the intercalation compound by immersing the film in ethanol and analyzed by ^{1}H NMR. In octylamine-intercalated graphite oxide without perfluoroalkyl groups, the *syn*/*anti* ratio increase with the increase of the amount of included acenaphthylene and reached 9 [29]. As the increase of the alkyl chain length of alkyl amines, the *syn*/*anti* ratio decreased. On the other hand, in $(\mathrm{FHEN})_{0.38}$GO, the *syn*/*anti* ratio was only 1.2 even at high acenaphthylene contents, which indicated that most of the dimers were formed via triplet excited state as shown in Fig. 10 [30]. This was ascribed to the weaker interaction between perfuloroalkyl group and acenaphthylene, facilitating the diffusion of excited acenaphthylene molecules, which lead to the increase of the formation of *anti*-isomer of acenaphthylene.

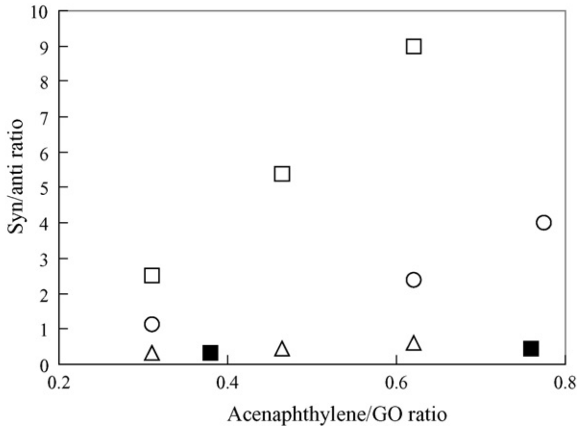

Fig. 10. *Syn*/*anti* ratios of acenaphthyene dimers formed in various intercalation compounds as a function of concentration of included acenaphthylene monomer. Open rectangle: $(\mathrm{C16})_{0.62}$GO, open circle: $(\mathrm{C12})_{0.62}$GO, open triangle: $(\mathrm{C8})_{0.62}$GO and filled rectangle: $(\mathrm{FHEN})_{0.38}$GO. From Refs. [29,30].

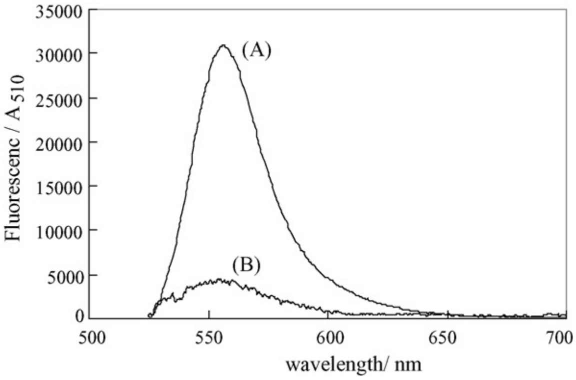

Fig. 11. Fluorescence spectra of rhodamine B co-intercalated in: (A) C16–$(\mathrm{FOESCl_3})$–GO and (B) C16–$(\mathrm{OSCl_3})$–GO. The C16/GO ratio was 3.0. From Ref. [20].

3.4. Enhancement of fluorescence of organic dyes in polyfluorinated environment

Matsuo et al. reported the enhancement of fluorescence from rhodamine B (hereafter abbreviated as RhB) molecules introduced in silylated graphite oxide containing perfluoroalkyl groups [20]. Fig. 11 shows the fluorescence spectra of RhB in silylated graphite oxide thin film containing perfluoroalkyl groups. In order to increase the solubility of them in chloroform/cyclohexane, *n*-hexadecylamine was intercalated into them and the resulting solution was cast to obtain film samples. The fluorescence was divided by the absorption at the wavelength of 510 nm, which was measured separately. The fluorescence from RhB in intercalation compound containing perfluoroalkyl chains was much larger than that without them. Both of the intercalation compounds possessed the similar interlayer spacings of about 5.0 nm, indicating the bilayer orientation of C16 molecules. This increase of emission can be ascribed to the perfluoroalky chains surrounding RhB molecules. Considering the previous report on the enhanced emission from neodymium complexes using perfluorinated ligand [31], the lower radiationless quenching by low vibrational C–F bonds would be responsible for the increase of fluorescence.

4. Summary

Various layered materials containing perfluoroalkyl groups were obtained by ion exchange method for layered materials with ion exchange capacity and by silylation technique for those possessing acidic hydroxyl groups. The nature of the interlayer space of them changed from hydrophilic to hydrophobic and therefore, organic molecules were introduced into the intercalation compounds by co-adsorption or exfoliation–restacking methods. The empty space surrounded by perfluoroalky chains where organic molecules are included showed unique properties such as weak interaction between perfluoroalkyl chains and guest molecules. The low vibrational C–F bonding in perfluoroalky groups reduced radiational quenching of rhodamine B molecules, accordingly enhanced the fluorescence from them. By utilizing these properties, the layered materials containing perfluoroalkyl groups are promising for adsorbents, matrices of photofunctional molecules, photochemical reaction media and so on.

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