



A novel nanocomposite material prepared by intercalating photoresponsive dendrimers into a layered double hydroxide

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ABSTRACT

A novel combination for an inorganic–organic nanocomposite material was demonstrated. Anthryl dendron, i.e., poly(amidoamine) dendron with an anthracene chromophore group at the focal point, was incorporated in the interlayer space of ZnAl–NO₃ type layered double hydroxide (LDH) through an anion-exchange reaction. The photoabsorption and fluorescence properties of the resulting material were different from those of the bare anthryl dendron molecule. It was suggested that the change in photochemical properties was due to the organization and π – π interaction of anthracene chromophores within the interlayer of the LDH.

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1. Introduction

Layered double hydroxides (LDHs), which consist of positively charged hydroxide layers, interlayer anions and water molecules, are widely known as host materials for the immobilization of guest species to create functional materials [1,2]. The chemical composition of LDH can be represented by the general formula $[M_{1-x}^{II}M_x^{III}(\text{OH})_2]^{x+}[A^{n-}]_{x/n} \cdot m\text{H}_2\text{O}$, where M^{II} and M^{III} represent divalent and trivalent metal cations, respectively, and Aⁿ⁻ is an exchangeable *n*-valent anion in the interlayer space, *x* is the charge density value of the hydroxide layer, and *m* is the number of water molecules in the LDH interlayer. Because the interlayer anions of LDH are exchangeable with external anions, various anionic guest species with specific properties can be loaded into the interlayer space [3,4]. In particular, it is interesting that the properties of some LDH-guest composite materials are reportedly different from those of bare guest species, due to the organization of guest molecules in the interlayer space and/or host–guest interactions [5–8].

On the other hand, well-defined regularly branched macromolecules of nanoscopic size called dendritic polymers (dendrons and dendrimers) have attracted attention of the science community in recent years, because dendritic polymers can be liberally functionalized by molecular design [9]. For example, fullerene-functionalized

dendrons (fullerodendrons) have been studied as materials for biologically active agents and nanoscopic photovoltaic cells [10–12].

Thus, inorganic–organic nanocomposite materials such as LDH and functionalized dendrimers are extremely interesting from the viewpoint of functional material design. However, although there have been only a few reports of nanocomposite materials of inorganic layered compounds and dendrimers to date, research on the hybridization of LDH and dendrimers has not explained the specific effects of the host–guest interactions and/or the organization of guest dendrimers in the interlayer space [13–18]. In particular, the effect of the organized-dendrimers in the LDH interlayers was not reported in this research. If such effects appeared in nanocomposite materials of inorganic compounds and dendrimers, a new strategy for material design could be developed. Accordingly, we report the first successful preparation of LDH containing photoresponsive dendrimers in the interlayer space through an ion-exchange reaction. ZnAl–NO₃ type LDH (M^{II} = Zn²⁺, M^{III} = Al³⁺, Aⁿ⁻ = NO₃⁻) and a photoresponsive dendrimer such as the poly(amidoamine) dendron, with an anthracene chromophore group at the focal point (anthryl dendron G1.5, Fig. 1), were employed in the present study. Furthermore, the photochemical properties of the resulting materials were investigated using UV–vis absorption and fluorescence spectroscopy.

2. Experimental section

2.1. Reagents

Special grade reagents were obtained from Tokyo Chemical Industry Co., Ltd., Kanto Kagaku Co., Ltd., Wako Pure Chemical

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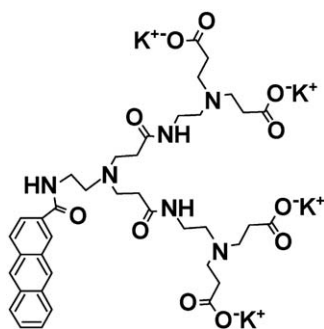


Fig. 1. Structural illustration of anthryl dendron G1.5.

Industries, Ltd., Nacalai Tesque, Inc., and Taimei Chemicals Co., Ltd., Japan, and were used as-received without further purification.

2.2. Synthesis of host and guest

ZnAl-NO₃ type LDH was prepared by the coprecipitation method, according to the methods proposed in previous reports [19,20]. An aqueous solution of 1 M (mol dm⁻³) metal nitrate (Zn²⁺/Al³⁺=2/1, Zn²⁺+Al³⁺=1 M; 42 cm³) was continuously added dropwise to a 10 M NaNO₃ aqueous solution (300 cm³) with stirring and N₂ bubbling at room temperature. The pH value of the mixed solution was controlled at pH 10 throughout the precipitation by the addition of 2 M NaOH aqueous solution. The precipitate was separated and washed several times with deionized water. The resulting white slurry was then collected by centrifugation and dried at 50 °C (NO₃-LDH).

Anthryl dendron G1.5 was prepared according to the reported method as follows [21–23]. A dendron, compound G0.0, which has an anthracene-modified focal point, was obtained by adding a methanol dispersion of methyl 2-anthracenecarboxylate to excess ethylenediamine followed by reaction for 1 d at 40 °C. Subsequent addition of methyl acrylate to the methanol solution of G0.0 followed by reaction for 3 d at 40 °C produced dendron G0.5. The two-step process was repeated to prepare anthryl dendron G1.5. Finally, four terminal groups were substituted for potassium tetracarboxylate by adding KOH methanol solution to a tetrahydrofuran solution of the product followed by reaction for 3 h at room temperature. The dissociation state of the anthryl dendron G1.5 against pH change in aqueous solution was examined by titration. One millimolar anthryl dendron aqueous solution (50 cm³) was titrated with 1 mM HCl aqueous solution.

2.3. Anion-exchange procedures

The anion-exchange reaction of LDH with anthryl dendron G1.5 was performed as follows. NO₃-LDH powder (100 mg) was dispersed into 1 M anthryl dendron aqueous solution (20 cm³) with pH previously adjusted to pH 5.5 using 13 M HNO₃ solution. To avoid contamination by CO₃²⁻ from CO₂ in the atmosphere by the protonation of CO₃²⁻ [24], the pH was adjusted to as low as possible without dissolution of the ZnAl type LDH [20]. The mixture was stirred for 1 h at room temperature and the orange-colored product was then collected by centrifugation and dried at 50 °C (Anth-LDH).

To study the difference in the photochemical properties between the dendron-loaded LDH and the dendron-unloaded one, a sample with anthryl dendron G1.5 adsorbed only on the external surface of LDH was prepared as follows. Anth-LDH powder (100 mg) was dispersed into 0.1 M Na₂CO₃ aqueous solution (20 cm³), and the mixture was stirred for 1 h at room

temperature. The cream-colored product was then collected by centrifugation and dried at 50 °C (ExSurf-LDH).

2.4. Characterization

¹H and ¹³C nuclear magnetic resonance (NMR) spectra were acquired using a JEOL JNM-AL 300 spectrometer, and a solution was made by dissolving anthryl dendron G1.5 in CD₃OD. Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectroscopic analysis was performed using a Bruker AUTOFLEX mass spectrometer using *trans*-3-Indoleacrylic acid as the matrix. X-ray powder diffraction (XRD) analyses were carried out on a Rigaku RINT2100/PC diffractometer with monochromated CuKα radiation (λ=1.5406 Å), using an operation voltage and current of 40 kV and 30 mA, respectively. Fourier transform infrared (FT-IR) spectra were measured on a JASCO FT/IR-350 Fourier transform infrared spectrometer in the range of 1000–4000 cm⁻¹ using the KBr pellet technique. Thermogravimetric-differential thermal analysis (TG-DTA) was performed using a Rigaku TAS100 instrument in the temperature range from room temperature to 800 °C with a 5 °C min⁻¹ heating rate in air, with α-Al₂O₃ used as the standard. The titration curve was recorded using a DKK-TOA HM-5S glass electrode pH meter. CHN elemental analyses were carried out using a Perkin Elmer 2400 Series II CHNS/O analyzer and a ThermoQuest FlashEA 1112 CHN-O analyzer. The metal and NO₃⁻ contents in the LDH samples were analyzed with a Thermo Fisher Scientific iCAP 6300Duo inductively coupled plasma (ICP) spectrometer and a Dionex DX-100 ion chromatograph, respectively. UV–vis diffuse reflectance spectra and UV–vis light absorption spectra were measured on a Shimadzu UV-2450 spectrophotometer. Fluorescence spectra of solid and liquid samples were measured on Hitachi F-4500 and JASCO FP-6600 spectrofluorometers, respectively.

3. Results and discussion

3.1. Synthesis of materials

¹H, ¹³C NMR and MALDI-TOF mass spectroscopies and elemental analysis revealed that the anthryl dendron G1.5 was successfully synthesized (data shown in Supplementary materials), with reference to the previous report [22,23]. Fig. 2 shows a pH titration curve of anthryl dendron G1.5. Anthryl dendron G1.5 is categorized as a heptaprotic base, which has seven stepwise dissociation constants K_{a1} – K_{a7} , and is regarded as a kind of amino acid, because it has four potassium carboxylic salts as terminal groups and three tertiary amines in branch (Fig. 1). Therefore, the isoelectric point could be determined as an inflection point when 200 cm³ of 1 mM HCl aqueous solution is added to the anthryl dendron G1.5 aqueous solution (1 mM, 50 cm³). Thus, it was revealed that the pH value at the isoelectric point was approximately 5.5, indicating that anthryl dendron exists as monovalent anions, neutral molecules and/or monovalent cations during the anion-exchange treatment at pH 5.5.

XRD patterns of NO₃-LDH, Anth-LDH, and ExSurf-LDH are shown in Fig. 3. The XRD pattern of NO₃-LDH displayed typical diffraction peaks based on a nitrate form of LDH indexed with rhombohedral symmetry (d_{003} =0.89 nm) [1,2,25]. The XRD patterns of Anth-LDH and ExSurf-LDH were also indexed with rhombohedral symmetry, and the basal spacings were estimated as 2.32 and 0.76 nm, respectively. The diffraction peaks corresponding to the basal spacing of Anth-LDH were shifted toward the lower 2θ side compared with those of the parent NO₃-LDH. The increase of the basal spacing was estimated to be approximately

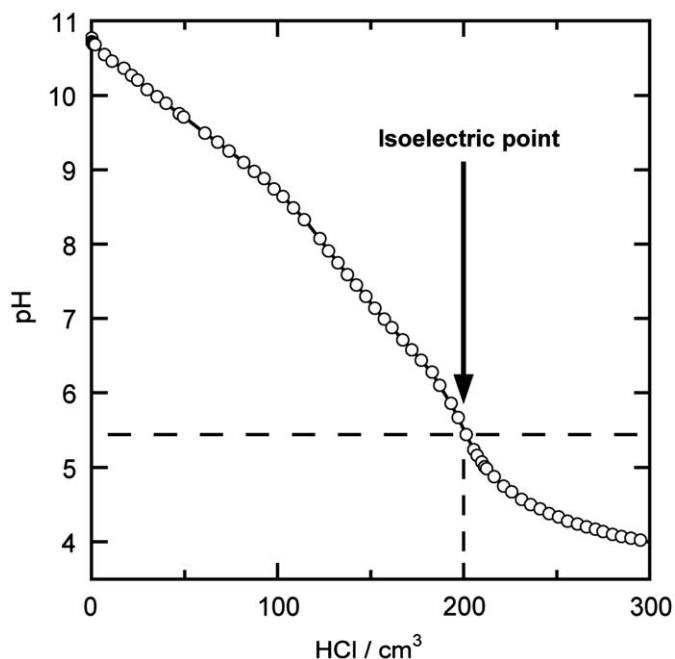


Fig. 2. Titration curve of anthryl dendron G1.5 aqueous solution.

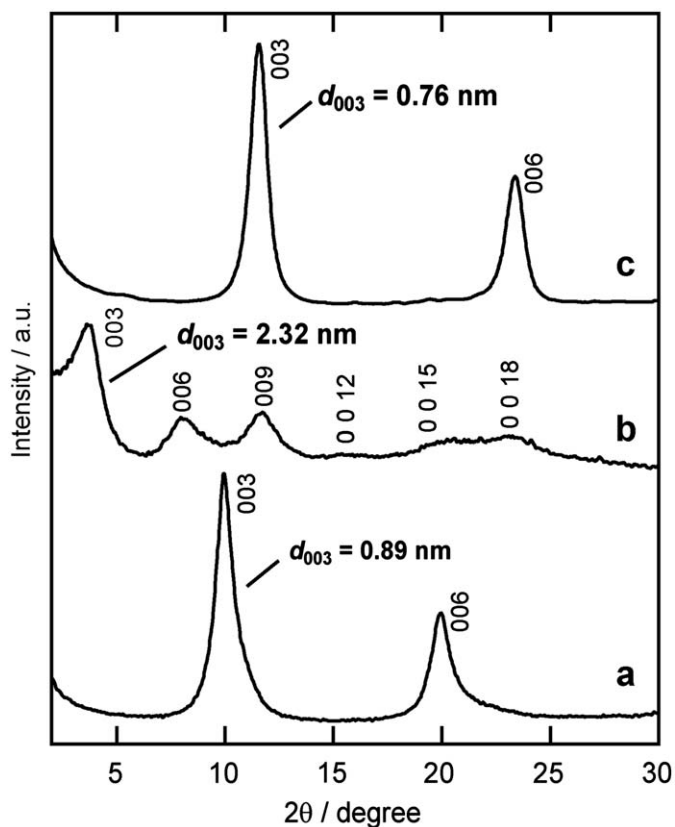


Fig. 3. XRD patterns of (a) NO_3 -LDH, (b) Anth-LDH, and (c) ExSurf-LDH.

1.43 nm, suggesting that anthryl dendron G1.5 was loaded into the interlayer space of LDH. The XRD pattern of ExSurf-LDH displayed typical diffraction peaks based on a carbonate form of LDH [26]. Since the interlayer region of LDH has extremely high affinity toward CO_3^{2-} , the anthryl dendrons in the interlayer were assumed to be exchanged with carbonate ions [27,28].

Evidence for the loading of anthryl dendron G1.5 into the interlayer space of LDH was also provided by FT-IR spectroscopy and TG-DTA. FT-IR spectra of LDH samples are shown in Fig. 4. The FT-IR spectrum of NO_3 -LDH showed absorption bands that were assigned to OH^- stretching vibration ($3600\text{--}3200\text{ cm}^{-1}$) of both the hydroxide layer and interlayer water molecules, and HOH bending vibration (1616 cm^{-1}) of the interlayer water. The interlayer NO_3^- gives a strong absorption band at 1383 cm^{-1} [29]. For the FT-IR spectrum of Anth-LDH, characteristic absorption bands were assigned as corresponding to amide NH stretching (3220 and 3076 cm^{-1}), alkyl CH stretching (2958 and 2831 cm^{-1}), amide I (1645 cm^{-1}), amide II (1550 cm^{-1}), RCOO^- antisymmetric stretching (1577 cm^{-1}), RCOO^- symmetric stretching (1414 cm^{-1}), OH bending and CO stretching of RCOOH (1323 and 1184 cm^{-1}), and anthracene groups (1462 cm^{-1}) [18,26,29,30], while the absorption band attributed to NO_3^- still remained in the spectrum. These absorption bands indicate that the anion-exchange procedure resulted in partial ion exchange and that anthryl dendron G1.5 is present in Anth-LDH. In the spectrum of ExSurf-LDH, interlayer CO_3^{2-} showed a stretching band at 1362 cm^{-1} [18,29]. Furthermore, shoulder bands assigned to CH stretching (2960 cm^{-1}), amide I (1635 cm^{-1}), and amide II (1550 cm^{-1}) of the dendron were observed, although the absorption bands attributed to the dendron were considerably weakened. These shoulder bands are probably due to the anthryl dendrons adsorbed on the external surface of the cream-colored ExSurf-LDH.

The TG-DTA curves of NO_3 -LDH (Fig. 5a) revealed typical thermal properties for a nitrate form of LDH [31]. On the other

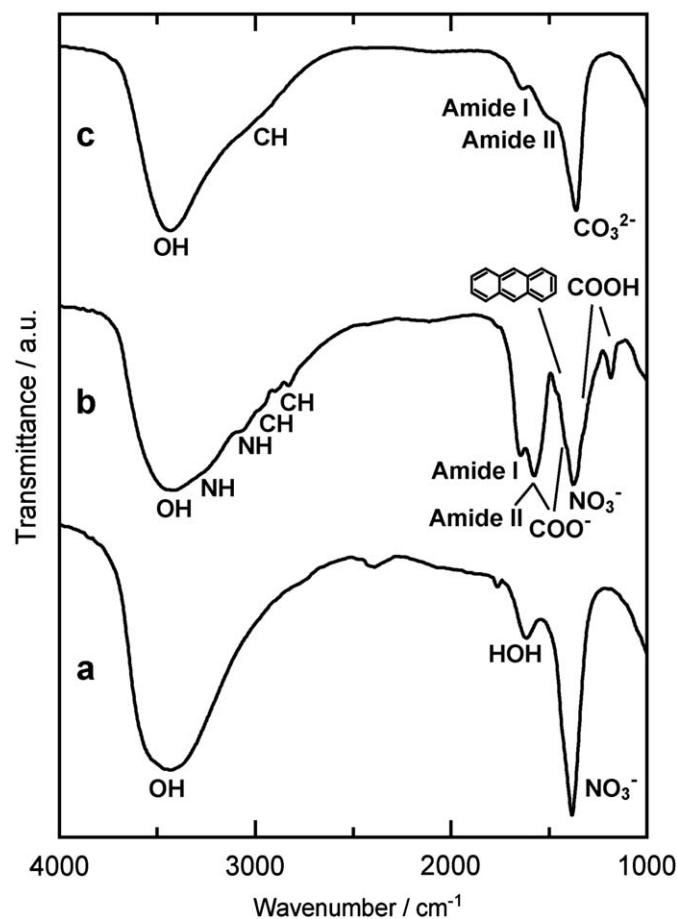


Fig. 4. FT-IR spectra of (a) NO_3 -LDH, (b) Anth-LDH, and (c) ExSurf-LDH.

hand, the TG-DTA curves of Anth-LDH (Fig. 5b) showed significant weight loss and exothermic peaks in the range of 240–520 °C. Similarly, the TG-DTA curve of ExSurf-LDH showed exothermic peaks in approximately the same temperature range, as shown in Fig. 5c. Moreover, the TG-DTA curves of pure solid anthryl dendron G1.5 and the dendron adsorbed on the surface of α -Al₂O₃ powder as a reference sample revealed weight loss and exothermic peaks in the range of 250–450 and 200–500 °C, respectively, (Supplementary materials: Fig. S1). Consequently, it was found that the weight loss and exothermic peaks around 240–520 °C observed for Anth-LDH were due to combustion of the dendron loaded in the interlayer of LDH.

From these results, it was concluded that anthryl dendron G1.5 was successfully encapsulated into the interlayer space of LDH, in addition to being adsorbed on the external surface of LDH through an anion-exchange reaction. The adsorbed dendrons on the external surface of LDH remained after treatment with the

Na₂CO₃ solution. The results of elemental analyses of the LDH samples are listed in Table 1. ICP analyses revealed that the Zn/Al molar ratios for Anth-LDH and ExSurf-LDH are nearly the same as that for NO₃-LDH, which indicates that the structure of the Zn–Al hydroxide layer did not change through the anion-exchange procedure in pH 5.5 aqueous solution. The C content obtained from CHN analysis of NO₃-LDH suggests that a small amount of CO₃²⁻ derived from CO₂ in the air was loaded in the LDH interlayer during the coprecipitation method and the subsequent anion-exchange procedure. The presence of NO₃⁻ and CO₃²⁻ was considered for estimation of the Anth-LDH composition, and it was assumed that the dendron existed as a monovalent anion form. In addition, the amount of dendrons adsorbed on the external surface was excluded from the estimation, because the amount was very small in the analysis of ExSurf-LDH. As a result, the amount of dendrons in Anth-LDH was estimated to be approximately 25% of the theoretical anion-exchange capacity of the host. For ExSurf-LDH, almost all positive charges of the basal layer would be countered by CO₃²⁻, because no NO₃⁻ in the sample was detected by ion chromatography. That is, the N content detected by CHN analyses was considered to be attributable to anthryl dendron adsorbed on the external surface, and the amount of the adsorbed dendron was estimated to be less than 0.003 per formula.

3.2. Photophysical properties

Anthracene and its derivatives have been widely known to exhibit photophysical and photochemical properties such as fluorescence; therefore, the UV–vis absorption and fluorescence properties of the samples were also examined. Fig. 6 shows UV–vis absorption spectrum of a 1×10^{-3} M anthryl dendron G1.5 aqueous solution at pH 5.5, and diffuse reflectance spectra of Anth-LDH powder and pure solid anthryl dendron G1.5. Compared to the aqueous solution of anthryl dendron G1.5, absorption bands of the Anth-LDH and the solid dendron in the range of 310–435 nm were significantly stronger, and new shoulders appeared at around 500 nm, probably due to anthracene aggregates [7,8]. The shoulder was particularly enhanced on the spectrum of anthryl dendron G1.5 solid, compared to Anth-LDH. Fig. 7 shows UV–vis diffuse reflectance spectra of the powder LDH samples of NO₃-LDH, Anth-LDH, and ExSurf-LDH. In the spectrum of NO₃-LDH, the absorption band in the range of 310–435 nm was very weak and no shoulder was observed at around 500 nm. Although the spectrum of ExSurf-LDH has a similar feature to that of Anth-LDH, the absorbance was very weak compared to that of Anth-LDH.

Fluorescence spectra (excited at 360 nm) for the 1×10^{-5} M anthryl dendron G1.5 aqueous solution at pH 5.5, Anth-LDH powder, ExSurf-LDH powder, and anthryl dendron G1.5 pure solid are shown in Fig. 8. The bare anthryl dendron G1.5 in aqueous solution and ExSurf-LDH powder had emission spectra with a maximum at around

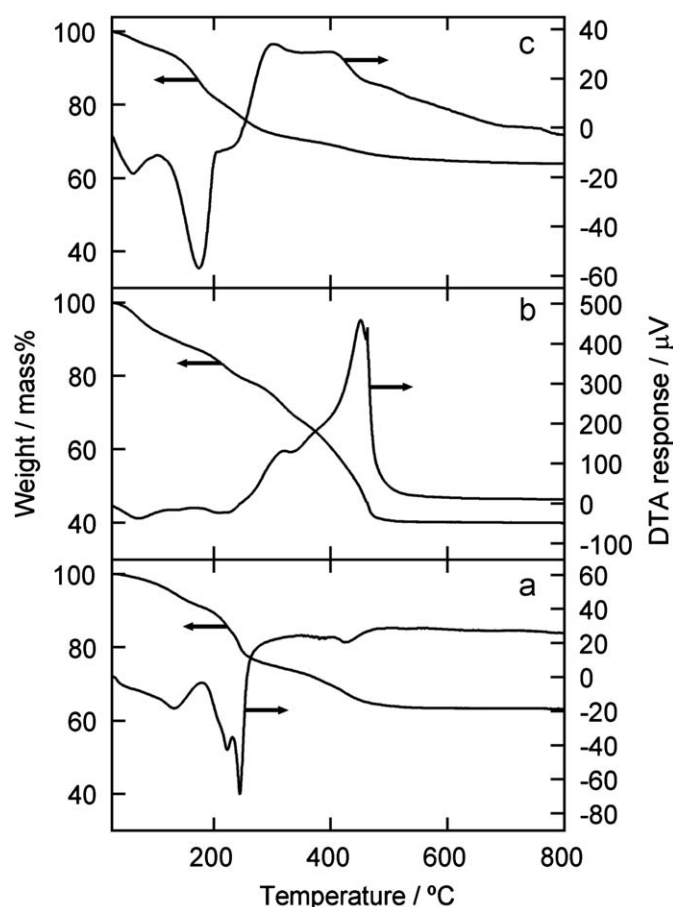


Fig. 5. TG-DTA curves of (a) NO₃-LDH, (b) Anth-LDH, and (c) ExSurf-LDH.

Table 1
Elemental analysis results for LDH samples.

Sample	Zn/Al	Elemental content (mass%)			Composition
		C	H	N	
NO ₃ -LDH	2.08	0.4	2.6	3.0	[Zn _{0.68} Al _{0.32} (OH) ₂](NO ₃) _{0.24} (CO ₃) _{0.035} · 0.40H ₂ O
Anth-LDH	2.07	22.6	4.5	4.7	[Zn _{0.67} Al _{0.33} (OH) ₂](NO ₃) _{0.09} (CO ₃) _{0.079} (G1.5 _{in}) _{0.083} · 0.53H ₂ O ^a
Surf-LDH	2.07	4.3	3.0	0.2	[Zn _{0.67} Al _{0.33} (OH) ₂](CO ₃) _{0.165} · 0.41H ₂ O · (G1.5 _{ex}) _{~0.003} ^b

^a The anthryl dendron in the interlayer was abbreviated to G1.5_{in}.

^b The anthryl dendron adsorbed on the external surface was abbreviated to G1.5_{ex}.

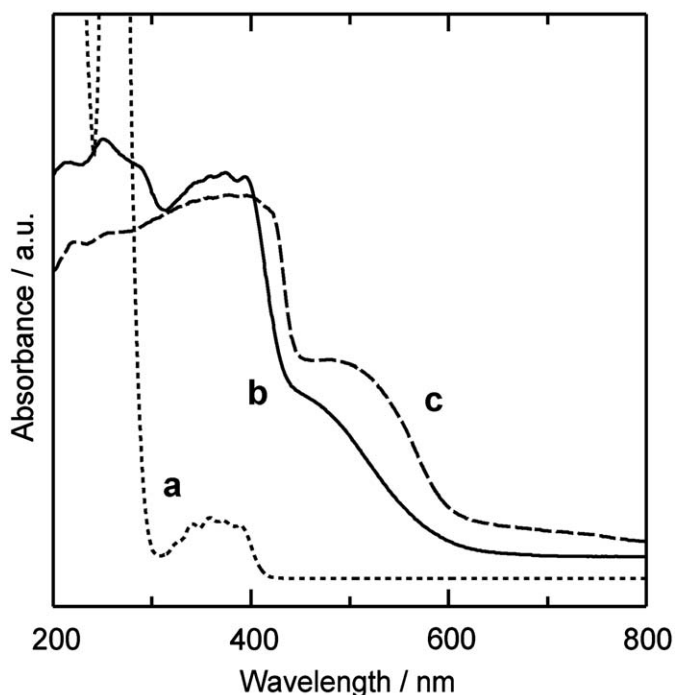


Fig. 6. UV-vis absorption spectrum of (a) 1×10^{-3} M anthryl dendron G1.5 aqueous solution at pH 5.5 (dotted line), and diffuse reflectance spectra of (b) Anth-LDH powder (solid line), and (c) pure solid of anthryl dendron G1.5 (broken line).

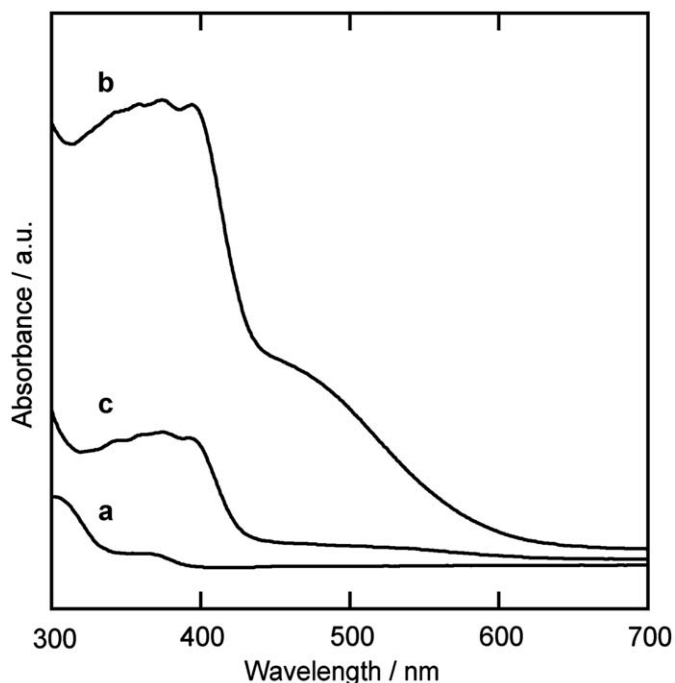


Fig. 7. UV-vis diffuse reflectance spectra of powder samples of (a) NO₃-LDH, (b) Anth-LDH, and (c) ExSurf-LDH.

450 nm, whereas Anth-LDH powder had an emission spectrum with a maximum at around 500 nm. In the case of the anthryl dendron G1.5 solid, the spectrum had a maximum at the longer wavelength side compared to the others and a broad peak at around 450 nm. It is well known that the photophysical and photochemical behavior of anthracene derivatives are dependent on the microenvironment surrounding the anthracene chromophore group [32,33]. According

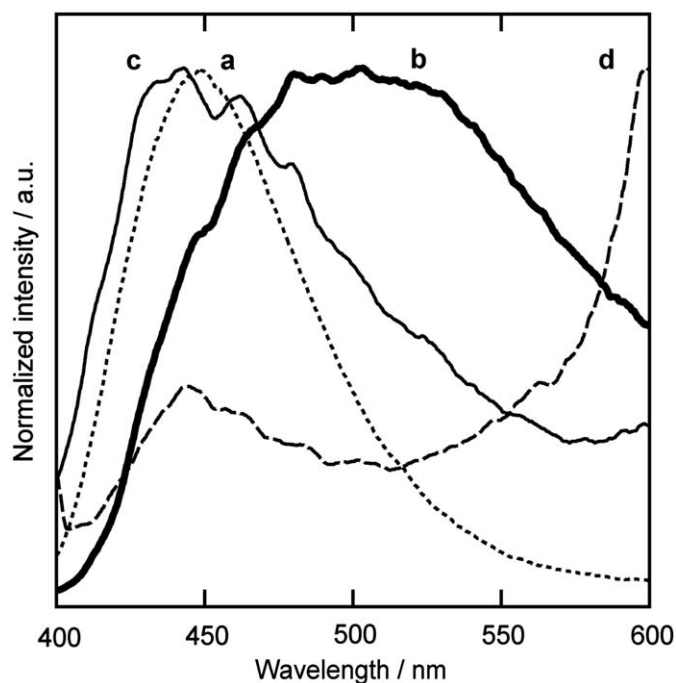


Fig. 8. Fluorescence spectra (excited at 360 nm) of (a) 1×10^{-5} M anthryl dendron G1.5 aqueous solution at pH 5.5 (dotted line), (b) Anth-LDH powder (bold line), (c) ExSurf-LDH powder (solid line), and (d) anthryl dendron G1.5 solid (broken line).

to the previous literature regarding the intercalation of 9-anthracene-carboxylate anion (9AC) into LDH, the anthracene chromophores interact with one another by π - π overlap in the interlayer space [8]. As a result, the absorption and emission spectra of the 9AC-LDH nanocomposite and bare 9AC in solvent are different to each other, in a similar manner to the present case. The emission peaks at around 450 nm are attributed to the bare chromophores that do not interact with each other, and the peaks at the longer wavelength side are attributed to the chromophores that interact by π - π overlap. Accordingly, the differences in the absorption and emission spectra between bare anthryl dendron G1.5 in aqueous solution and Anth-LDH strongly indicate that the organization of the anthryl dendron G1.5 results in interaction between the π electrons of anthracene chromophores in the interlayer of LDH. On the other hand, the chromophores on the LDH surface can exist far apart from each other, resulting in less π - π overlap. The chromophores are more closely packed in the anthryl dendron G1.5 solid than those in Anth-LDH, resulting in a large number of π - π overlaps. Furthermore, a portion of the chromophores that are not interacting with each other in the anthryl dendron G1.5 solid are probably responsible for the broad peak emission at around 450 nm.

On the basis of these results, a schematic image of the dendrons loaded in the interlayer is given in Fig. 9. It was found that the structure of the hydroxide layer did not change through an anion-exchange procedure and that the dendrons in the interlayer exist as monovalent anions. Considering that the thickness of the ZnAl type LDH hydroxide layer is 0.48 nm [6,26], the interlayer distance was calculated to be 1.84 nm. Anthryl dendron G1.5 can be regarded as a planar molecule, and the maximum size of the anthryl dendron G1.5 molecule is estimated to be 2.3 nm long, 2.1 nm wide, and 0.4 nm thick. Therefore, the molecular length and width are too large for the anthryl dendron G1.5 to load into the interlayer space with its molecular plane perpendicular to the hydroxide layer. Furthermore, the thickness could be too thin for anthryl dendron G1.5 to exist in the interlayer with its molecular plane

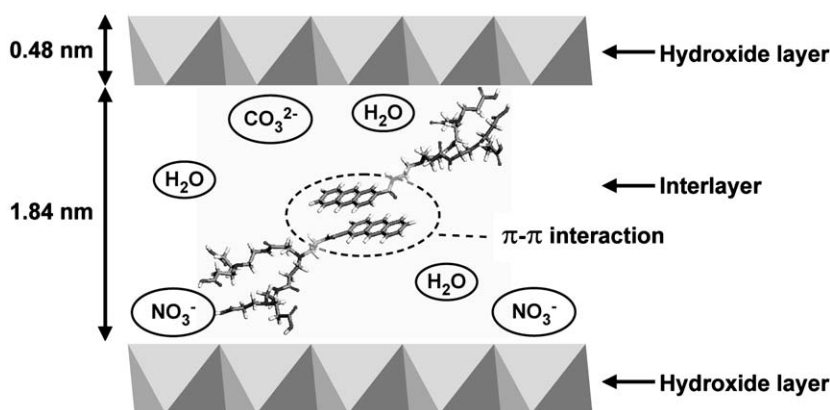


Fig. 9. Schematic image of anthryl dendrons loaded into the interlayer of LDH.

parallel to the hydroxide layer. In addition, the anthracene chromophores were overlapped each other by π - π interaction, as evidenced by the UV-vis absorption and fluorescence spectra. Accordingly, a possible model was depicted, where anthryl dendron G1.5s are arranged in the interlayer with slight tilting of the molecular plane to the hydroxide layer to form a bilayer of anthracene chromophores facing each other.

4. Conclusion

In conclusion, a novel material of LDH containing poly(ami-damine) dendron with an anthracene chromophore group at the focal point was successfully prepared by ion-exchange reaction. The photoabsorption and fluorescence properties of the resulting material were different from those of the bare anthryl dendron molecule. The differences suggest that intercalation resulted in interaction between the π electrons of the anthracene chromophores of dendrons by overlapping with each other in the interlayer space of LDH. This study is the first investigation of a functionalized dendritic polymer loaded into the interlayer of LDH that exhibits specific properties induced by the organization of dendritic polymers in the interlayer space. As the dendron employed in this work has an anthracene group as a guest dendritic polymer, it is highly probable that LDH can be combined with other dendritic polymers that possess various functional groups. Moreover, it must be stressed that the present work has proven that the anthracene chromophores of dendrons interact with each other in the interlayer space of LDH in analogy with just anthracene molecules (9AC) in the LDH, despite the large difference in molecular size between the dendron and 9AC. Therefore, it is expected that interesting effects appear in such nanocomposite materials and that such a strategy to design functional materials by combination of LDHs with various types of dendrimers will be very valuable. Further work is in progress to synthesize other types of nanocomposite materials, such as LDH-fullerodendron, in the hope that these materials exhibit desirable photoelectrochemical properties.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2009.12.016.

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