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INTERCALATION OF 8-HYDROXYQUINOLINE INTO Al-SMECTITES BY SOLID-SOLID REACTIONS

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Abstract—Tris(8-hydroxyquinoline)aluminum (III) complexes (Alq_3), one of the molecules studied most widely for organic light-emitting devices, were formed in the interlayer spaces of smectites by solid-solid reactions between Al-smectites (Al-montmorillonite and Al-synthetic saponite (Sumecton)) and 8-hydroxyquinoline (8Hq) at room temperature. The intercalation of 8-hydroxyquinoline molecules into Al-smectites was demonstrated by powder XRD, FTIR, DTA, TG, TG-MS, and chemical analysis. The coordination of the ligand to the interlayer Al cations was proved by FTIR, UV-Vis, and photoluminescence spectroscopies. The luminescence intensity of Alq_3-Sumecton was much greater than that of Alq_3-montmorillonite, and this was ascribed to the very small amount of quenching impurities in Sumecton.

Key Words—8-Hydroxyquinoline, Montmorillonite, Solid-State Intercalation, Sumecton SA, Synthetic Saponite, Tris(8-hydroxyquinoline)aluminum(III) Complex.

INTRODUCTION

The intercalation of guest species into layered inorganic solids has attracted considerable attention from a wide range of scientific and practical viewpoints (Whittingham, 1982). Among possible host materials, smectites possess a number of attractive features such as the swelling behavior, ion exchange property, adsorptive property and large surface area (Van Olphen, 1977) for organizing guest species. Synthesis, characterization and properties of smectite-organic intercalation compounds have been reported extensively (Theng, 1974; Ogawa and Kuroda, 1995, 1997). During the course of the present study on clay-organic interactions, we found that solid-solid reactions are effective at introducing organic species into the interlayer spaces of smectites. So-called solid-solid reactions including mechanochemical adsorption, which occur between powders in the solid state, have been used because of the ease of operation, the option of preparing compounds which are not accessible from solutions, and so on (Patil *et al.*, 1984; Toda *et al.*, 1987). Solid-state intercalation of organic guest species into layered clay minerals (Ogawa *et al.*, 1989, 1990, 1991, 1997; Bujdák and Slosiariková 1992), layered zirconium phosphate (Clearfield and Troup, 1970), and zeolites (Lázár *et al.*, 1994) has been reported as a way of utilizing host structures. Solid-state intercalation can be split into two stages; one is the diffusion of guest species from the outer surfaces of guest solids and the other is the penetration of the guest species into the interlayer spaces (Rastogi *et al.*, 1977).

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We have successfully introduced complex ions into the interlayer space of montmorillonite by the solid-state intercalation of ligands and the *in situ* formation of complexes. The intercalation of 2,2′-bipyridine, 4,4′-bipyridine and 1,2-di(4-pyridine)ethylene and crown ethers into montmorillonite through the formation of complexes has already been reported (Ogawa *et al.*, 1991, 1997; Khaorapapong *et al.*, 2000, 2001). The formation of complexes on solid surfaces is worth investigating since the immobilization of complexes on solid surfaces is important in relation to the construction of functional surfaces as well as novel low-dimensional nanomaterials (Ozin, 1989).

Here, we report the intercalation of 8-hydroxyquinoline (molecular structure is shown in Figure 1a) into the interlayer spaces of Al-exchanged smectites. Tris(8-hydroxyquinoline)aluminum(III) complexes (structure shown in Figure 1b) is one of the compounds studied most widely as an organic light-emitting material (Tang and Van Slyke, 1987). Various light-emitting devices have been constructed from Alq_3 (Tang *et al.*, 1989; Kido *et al.*, 1995; Sheats *et al.*, 1996; Van Slyke *et al.*, 1996; Kido and Iizumi, 1998). Because the optical properties are affected by the crystal structures and molecular packings of Alq_3 (Brinkmann *et al.*, 2000), the immobilization of Alq_3 in solid matrices may affect the light-emitting properties. Therefore, the introduction of Alq_3 into solid matrices is worth investigating. Because Alq_3 is an ionically neutral species, the intercalation of pre-synthesized Alq_3 into the interlayer spaces of smectites is difficult. In the present study, therefore, we performed the solid-state reaction between Al-smectites and 8-hydroxyquinoline

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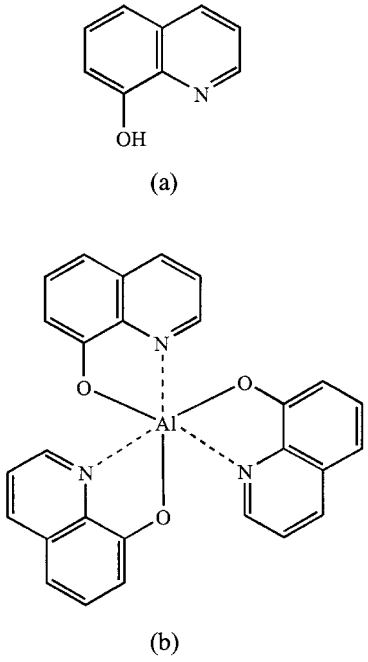


Figure 1. The molecular structures of (a) 8-hydroxyquinoline (8Hq) and (b) tris(8-hydroxyquinoline)aluminum(III) complex (Alq_3).

in order to achieve Alq_3 complexes in the interlayer spaces of smectites.

EXPERIMENTAL

Materials

Two smectites, synthetic Na-saponite (Sumecton SA; the reference clay sample of the Clay Science Society of Japan, JCSS-3501, synthesized hydrothermally by Kunimine Industries Co.) and Na-montmorillonite (JCSS-3101, Kunipia F, obtained from Tsukinuno mine, Japan) were used as the host materials. The cation exchange capacities (CEC) of the clays were 70 and 120 meq/100 g of clay for Na-Sumecton (Ogawa *et al.*, 1994) and Na-montmorillonite (Sugahara *et al.*, 1984), respectively. The 8-Hq (analytical grade) and aluminum chloride were obtained from Kanto Chemical Co. Inc. and used without further purification.

Sample preparation

Al-Sumecton and Al-montmorillonite were prepared by a conventional ion exchange method. Powders of Na-smectites were mixed with a fresh aqueous solution of aluminum chloride and the mixtures were stirred at room temperature for 1 day. After the ion exchange, the resulting solids were collected by centrifugation and washed with deionized water repeatedly until a negative $AgNO_3$ test was obtained. The amounts of Al, determined by ICP, were 60 and 87 meq/100 g of clay for Na-Sumecton and Na-montmorillonite, respectively. Quantitative exchange with Al cations did not occur because of partial exchange with protons due to the fact that the pH values of the supernatants after the ion exchange reaction (2.5–3.0) as well as the starting solution (3.3) were low. The intercalation of 8Hq into Al-smectites was achieved via solid-solid reactions according to the method described previously by Ogawa *et al.* (1991). The mixtures of the hosts and guest species were ground manually using an agate mortar and pestle at room temperature for 2–3 min. The molar ratio of 8Hq to the interlayer Al cation was 3:1. The actual amounts for the montmorillonite system were 0.6004 g (montmorillonite) and 0.0760 g (8Hq) and those for the Sumecton were 0.6063 g (Sumecton) and 0.0530 g (8Hq). After the solid-solid reactions, the intercalation compounds were washed repeatedly with ethanol.

Characterization

Powder X-ray diffraction (XRD) data were collected on a Mac Science MXP^3 diffractometer using monochromatic CuKα radiation. Visible absorption spectra of the samples were recorded on a Shimadzu UV-3101PC spectrophotometer. Diffuse reflectance spectra of the solid samples were collected using an integrated sphere. Infrared (IR) spectra of the samples were recorded on a Perkin Elmer Spectrum One FTIR spectrophotometer by the KBr disk method. Thermogravimetric-differential thermal analysis (TG-DTA) curves were recorded on a Mac Science TG-DTA 2000S instrument at a heating rate of 10°C min^{-1} under a dry-air atmosphere using α-alumina (α-Al_2O_3) as a standard material. Thermogravimetric-mass spectroscopy (TG-MS) analysis was performed on a Rigaku Thermo plus MS/IF (a TG model) equipped with a Shimadzu GCMS-QP5050A gas chromatograph mass spectrometer at a heating rate of 10°C min^{-1} under a He flow. Luminescence spectra were recorded on a Hitachi F-4500 fluorospectrophotometer in the wavelength range 400–650 nm with the excitation at 373 nm. The amounts of 8Hq were determined by CHN analysis (Perkin Elmer PE-2400II). The amounts of Al were determined by inductively coupled plasma emission spectroscopy (ICP-ES) (Nippon Jarrell-Ash ICAP-575 Mark II).

RESULTS AND DISCUSSION

Powder XRD patterns of the products prepared by the reactions between Al-smectites and 8Hq are shown in Figure 2 together with those of Al-smectites. Hereafter, the samples are referred to as Al-smectites-8Hq. Al-montmorillonite-8Hq gave sharp XRD peaks (Figure 2b), with a basal spacing of ~1.7 nm. Further increase in the basal spacing was not observed when a large excess of 8Hq was added. By subtracting the thickness of the silicate layer (~1.0 nm) from the

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observed basal spacing, the gallery height was determined to be ~0.7 nm. The XRD pattern of 8Hq powders was measured (not shown) and the strong peaks were located at d = 0.94, 0.62, 0.38 and 0.31 nm. The XRD pattern of Al-montmorillonite-8Hq did not show any peaks due to 8Hq. Al-montmorillonite-8Hq was heated at 200°C for 1 h in air. The basal spacing of the heat-treated product was very similar to that of the original sample, supporting the intercalation of 8Hq. It was reported that the basal spacings of the Ni(II)- and Cu(II)-montmorillonite-8Hq intercalation compounds were 1.76 and 1.61 nm, respectively (Labhasetwar and Shrivastava, 1995), being approximately consistent with the present result. On the other hand, it was also reported that Na- and Ca-montmorillonites take up 8Hq. However, the basal spacings of those products are smaller than that of our product and some of the cations were released from the products (Ferreiro *et al.*, 1988).

The C and N contents of Al-montmorillonite-8Hq were 11.4% and 1.4%, respectively. The C:N ratio (9.4:1) of the product is in good agreement with that of the 8Hq molecule (9:1). The ratio of adsorbed 8Hq to interlayer Al cation was estimated to be ~3:1, based on the C content.

The TG-DTA curves of Al-montmorillonite-8Hq are shown in Figure 3 together with those of Al-montmorillonite and 8Hq. The endothermic peaks due to the melting and vaporization of 8Hq at ~75 and 185°C were absent from the DTA curve of Al-montmorillonite-8Hq, suggesting that no unreacted 8Hq molecules were present in the product. The endothermic reaction, starting from room temperature, which accompanied a weight loss, was ascribed to desorption of adsorbed water. Because the starting materials were ground at room temperature under ambient conditions, a small amount of adsorbed H_2O should reside on the surface. Previous papers reporting an effective use of DTA-MS analysis of organic-clay systems (Yariv, 1990, 1991) prompted us to perform TG-MS analysis of the present system. The TG-MS analysis (He flow) indicated that the gas evolved at 57°C was water. The mass spectra observed at temperatures >300°C showed peaks due to the ligand, suggesting the decomposition of Alq_3. In the TG curve (Figure 3b), the weight losses were observed in the temperature range 300–800°C. In the corresponding DTA curve (Figure 3e), three exothermic peaks were observed at the temperature range. The exothermic peaks were ascribed to the oxidative decomposition of coordinated 8Hq, although the detailed reaction at each temperature is difficult to elucidate. These observations confirm the intercalation of 8Hq into the interlayer space of Al-montmorillonite.

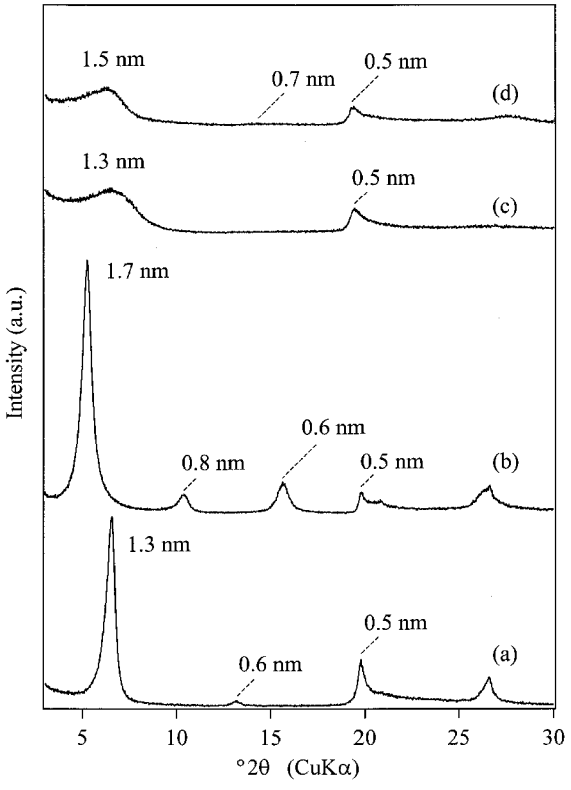


Figure 2. XRD patterns of (a) Al-montmorillonite, (b) Al-montmorillonite-8Hq, (c) Al-Sumecton, and (d) Al-Sumecton-8Hq.

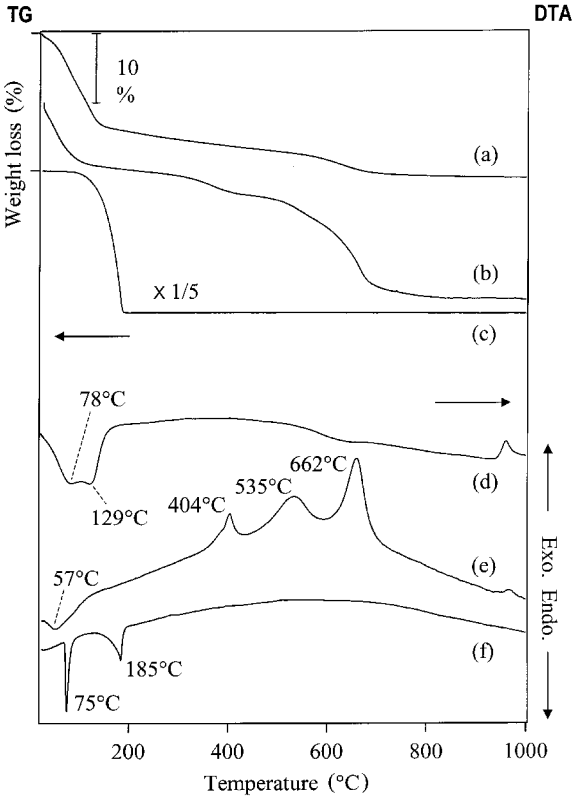


Figure 3. TG and DTA curves of (a,d) Al-montmorillonite, (b,e) Al-montmorillonite-8Hq, and (c,f) 8Hq, respectively.

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In order to examine the adsorbed states of 8Hq, the UV-Vis, IR and luminescence spectra of Al-montmorillonite-8Hq were recorded. In the FTIR spectrum of the product (Table 1), the absorption bands characteristic of 8Hq *e.g.* the C−H out-of-plane bending modes with strong relative intensities at 742, 781 and 818 cm^{-1} (Marchon *et al.*, 1986) were observed. The bands were shifted slightly towards higher wavenumbers, which proves the interactions between 8Hq and Al-montmorillonite. Compared with the characteristc absorption bands ascribable to Alq_3 *e.g.* the bands at 752, 789 and 825 cm^{-1} (Halls and Aroca, 1998), the slight shifts of the bands observed for Al-montmorillonite-8Hq strongly suggest the formation of coordination complexes of 8Hq with the interlayer cations. The FTIR spectra did not show any additional absorption bands due to decomposed species, confirming that there was no decomposition of 8Hq.

The diffuse reflectance absorption spectrum of Al-montmorillonite-8Hq is shown in Figure 4a together with those of 8Hq and Alq_3. In the spectrum of Al-montmorillonite-8Hq, an absorption band was observed at ~371−376 nm, and the band was not observed for the absorption spectra of Al-montmorillonite (not shown) and 8Hq (Figure 4c). The absorption band of Alq_3 in a dilute chloroform solution (concentration: 1.0×10^{-6} M) appears at 389 nm (Papadimitrakopoulos *et al.*, 1996) and that of sublimed Alq_3 thin film at 390 nm (Brinkmann *et al.*, 2000). The absorption band of Alq_3 powders appeared at 392 nm (Figure 4d). Consequently, the band observed for Al-montmorillonite-8Hq can be ascribed to Alq_3 formed in the interlayer space of montmorillonite, which is consistent with the photoluminescence spectra described below.

In the photoluminescence spectrum of Al-montmorillonite-8Hq (Figure 4a), weak luminescence was observed at ~521 nm, supporting the formation of Alq_3. The luminescence of Alq_3 appears at 514 nm in a methanol solution (Brinkmann *et al.*, 2000), 519 nm in a thin film, and 510 nm in poly(vinylcarbazole) (Higginson *et al.*, 1998). The luminescence of Alq_3 powders appears at 522 nm (Zhang *et al.*, 1996). The low intensity of the luminescence is considered to be caused by the quenching by Fe in montmorillonite. It is well known that the luminescence of some dyes adsorbed on montmorillonite and related natural clays is effectively quenched by Fe (Ogawa and Kuroda, 1995). This is supported by comparison of the luminescence intensity with that of the Sumecton system.

Taking the molecular size of Alq_3 (Brinkmann *et al.*, 2000; Curioni *et al.*, 1998), and the observed basal spacing (~0.7 nm), the Alq_3 complexes formed should take a monolayer arrangement in the interlayer space. This means that the ligand 8Hq molecules form a bilayer arrangement. Because Alq_3 is ionically neutral, the negative charge of montmorillonite should be compensated by protons derived from 8Hq.

It is worth noting that the complexes formed in the interlayer space of montmorillonite are relatively resistant to washing with ethanol. Al-montmorillonite-

Table 1. Wavenumbers (cm^{-1}) of IR bands of the products and their assignments.

Assignment	8Hq*	Alq_3**	Al-montmorillonite-8Hq	Al-Sumecton-8Hq
Ring stretching	1625 1593	1605	1607	1606
Ring stretching	1580	1580	1583	1583
Ring stretching	1509	1539	1561	1561
Ring stretching	1499	1500	1502	1503
Ring stretching	1473	1473	1473	1474
Ring stretching	1434	1425	1421	1421
+ CH bending	1410	1403	1402	
CH bending	1398	1386	1384	1385
+ Ring stretching	1380			
CH bending +	1372	1328	1325	1327
Ring stretching	1355			
CH bending	1286	1310	1307	1313
CH bending	1257	1282	1274	1274
CH stretching +	1245	1245	–	–
CH bending				
CH stretching +	1223	1230	1230	1230
CH bending				
C−O stretching +	1100	1116	–	–
CH bending				
CH wag	818	825	824	824
Ring deformation	807	806	805	805
CH wag	781	789	–	788
CH wag	742	752	754	752

* (Marchon *et al.*, 1986)
** (Halls and Aroca, 1998)

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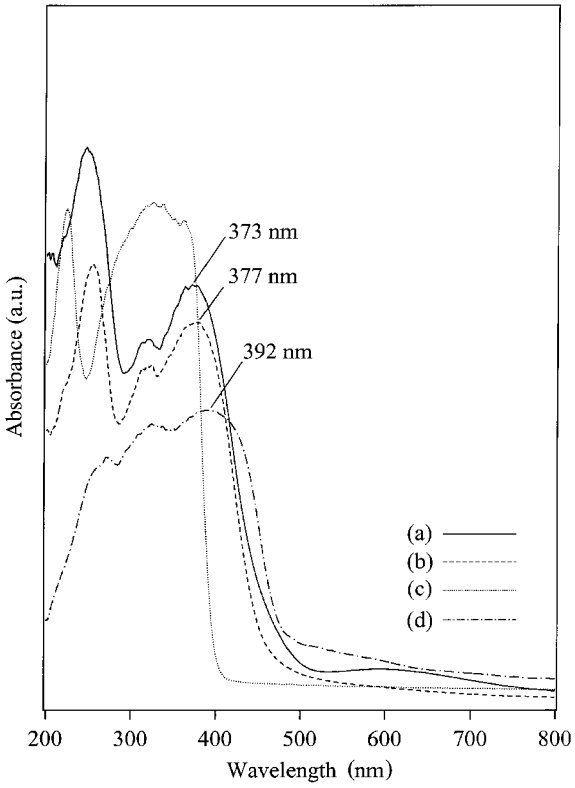


Figure 4. Diffuse reflectance absorption spectra of (a) Al-montmorillonite-8Hq, (b) Al-Sumecton-8Hq, (c) 8Hq and (d) Alq_3.

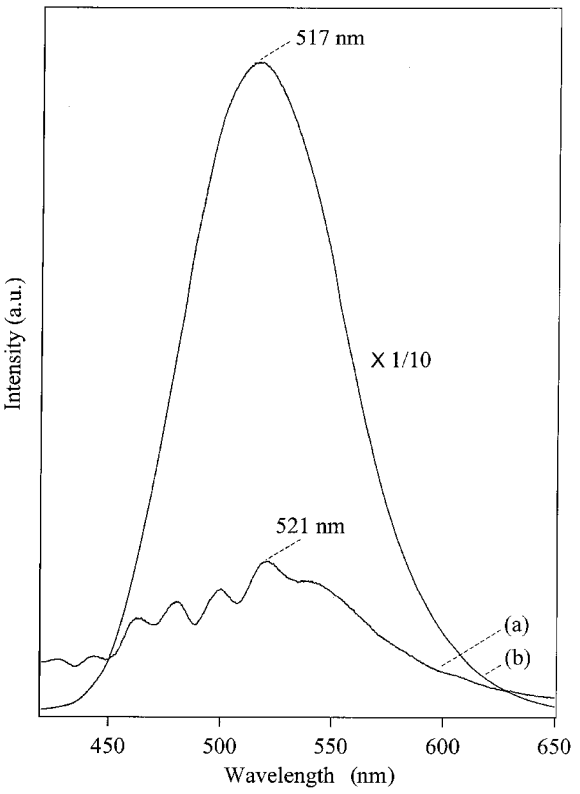


Figure 5. Luminescence spectra of (a) Al-montmorillonite-8Hq and (b) Al-Sumecton-8Hq.

8Hq was washed five times with ethanol at room temperature. A small amount of Alq_3 was desorbed by the washing as evidenced by the luminescence spectra of the supernatant liquids, for which the luminescence band due to Alq_3 was observed at 515 nm. The amount of desorbed Alq_3 was so small that the chemical composition of the solid did not change significantly. The CHN data of the washed products are shown in Table 2. The resistance to washing is worth noting as a measure of the present complexation in montmorillonite.

When Al-Sumecton was employed as the host material, the intercalation of 8Hq and formation of the Alq_3 complex was also proven by the XRD pattern, thermal analysis data, FTIR, diffuse reflectance absorption and luminescence spectra. The basal spacing of Al-Sumecton-8Hq is 1.5 nm (Figure 2d), indicating the expansion of the gallery height by ~0.5 nm. The gallery height is smaller than that of Al-montmorillonite-8Hq, suggesting a different orientation or arrangement of the interlayer guest species. The shifts in the IR bands to the wavenumbers higher than those for 8Hq were also observed for Al-Sumecton-8Hq (Table 1), supporting the intercalation of 8Hq molecules.

The diffuse reflectance UV-Vis spectrum of Al-Sumecton-8Hq showed an absorption band at the wavelength 377 nm. This band was slightly different from that (373 nm) observed for Al-montmorillonite-8Hq, suggesting that the microenvironments of Alq_3 formed in the interlayer space of Sumecton are different from those of Al-montmorillonite-8Hq. Because the CECs of Sumecton and montmorillonite used in the present study are 70 and 120 meq/100 g clay, respectively, the proximity of the adjacent complexes should be different. Consequently, the packing of the Alq_3 formed varied, giving the slight spectral difference.

The most notable feature of the Sumecton system is the intense luminescence. The luminescence spectrum of Al-Sumecton-8Hq (Figure 5b) showed a very intense luminescence peak centered at 517 nm. The luminescence intensity is 40 times greater than that observed for Al-montmorillonite-8Hq. As described earlier, it is thought that the impurities such as Fe in montmorillonite quenched the luminescence of Alq_3. The amount of quenching impurities in Sumecton is very small, so intense luminescence was observed for Al-Sumecton-8Hq.

Table 2. Chemical compositions of the products.

Host	C (mass %)	N (mass %)	C:N
Montmorillonite			
Before washing	11.4	1.4	9.4:1
After washing	10.8	1.3	9.3:1
Sumecton			
Before washing	4.7	0.6	9.0:1
After washing	1.7	–	–

–: Negligible

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CONCLUSIONS

8-Hydroxyquinoline was intercalated into the interlayer spaces of Al-smectites by solid-solid reactions at room temperature. The intercalated 8-hydroxyquinoline formed tris(8-hydroxyquinoline)aluminum(III) complexes in the interlayer spaces of smectites. When synthetic saponite (Sumecton) was used as the host material, intense luminescence of the complexes was observed. The wavelength of the UV-Visible and luminescence bands of the complexes varied slightly depending on the hosts, indicating the different microstructures including molecular packing of the complexes in the intercalation compounds. Appropriate selection of host materials, interlayer cations, and guest species as a ligand leads to a strong possibility of incorporating highly functional neutral complexes in the interlayer region by this solid-state intercalation.

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REFERENCES

Brinkmann, M., Gadret, G., Muccini, M., Taliani, C., Masciocchi, N. and Sironi, A. (2000) Correlation between molecular packing and optical properties in different crystalline polymorphs and amorphous thin films of *mer*-tris(8-hydroxyquinoline)aluminum(III). *Journal of American Chemical Society*, **122**, 5147–5157.

Bujdák, J. and Slosiariková, H. (1992) The reaction of montmorillonite with octadecylamine in solid and melted state. *Applied Clay Science*, **7**, 263–269.

Clearfield, A. and Troup, J.M. (1970) Ion exchange between solids. *Journal of Physical Chemistry*, **74**, 2578–2580.

Curioni, A., Boero, M. and Andreoni, W. (1998) Alq_3: ab initio calculations of its structural and electronic properties in neutral and charged states. *Chemical Physics Letters*, **294**, 263–271.

Ferreiro, E.A., De Bussetti, S.G. and Helmy, A.K. (1988) Sorption of 8-hydroxyquinoline by some clays and oxides. *Clays and Clay Minerals*, **36**, 61–67.

Halls, M.D. and Aroca, R. (1998) Vibrational spectra and structure of tris(8-hydroxyquinoline)aluminum(III). *Canadian Journal of Chemistry*, **76**, 1730–1736.

Higginson, K.A., Zhang, X.-M. and Papadimitrakopoulos, F. (1998) Thermal and morphological effects on the hydrolytic stability of aluminum tris(8-hydroxyquinoline) (Alq_3). *Chemistry of Materials*, **10**, 1017–1020.

Khaorapapong, N., Kuroda, K., Hashizume, H. and Ogawa, M. (2000) Solid state intercalation of 4,4-bipyridine into the interlayer space of montmorillonites. *Molecular Crystals and Liquid Crystals*, **341**, 351–356.

Khaorapapong, N., Kuroda, K., Hashizume, H. and Ogawa, M. (2001) Solid-state intercalation of 4,4-bipyridine and 1,2-di(4-pyridine)ethylene into the interlayer spaces of Co(II)-, Ni(II)-, and Cu(II)-montmorillonites. *Applied Clay Science*, **19**, 69–76.

Kido, J. and Iizumi, Y. (1998) Fabrication of highly efficient organic electroluminescent devices. *Applied Physics Letters*, **73**, 2721–2723.

Kido, J., Kimura, M. and Nagai, K. (1995) Multilayer white light-emitting organic electroluminescent device. *Science*, **267**, 1332–1334.

Labhasetwar, N.K. and Shrivastava, O.P. (1995) Intercalation compounds of Cu^{2+} and Ni^{2+}-exchanged montmorillonite clay with 8-hydroxyquinoline. *Journal of the Chinese Chemical Society*, **42**, 67–70.

Lázár, K., Pál-Borbély, G., Beyer, H.K. and Karge, H.G. (1994) Solid-state ion exchange in zeolites. *Journal of Chemical Society, Faraday Transactions*, **90**, 1329–1334.

Marchon, B., Bokobza, L. and Cote, G. (1986) Vibrational study of 8-quinolinol and 7-(4-ethyl-1-methyloctyl)-8-quinolinol (Kelex 100), two representative members of an important chelating agent family. *Spectrochimica Acta*, **42A**, 537–542.

Ogawa, M. and Kuroda, K. (1995) Photofunctions of intercalation compounds. *Chemical Reviews*, **95**, 399–438.

Ogawa, M. and Kuroda, K. (1997) Preparation of inorganic-organic nanocomposites through intercalation of organoammonium ions into layered silicates. *Bulletin of the Chemical Society of Japan*, **70**, 2593–2618.

Ogawa, M., Kuroda, K. and Kato, C. (1989) Preparation of montmorillonite-organic intercalation compounds by solid-solid reactions. *Chemistry Letters*, 1659–1662.

Ogawa, M., Handa, T., Kuroda, K. and Kato, C. (1990) Formation of organoammonium-montmorillonites by solid-solid reactions. *Chemistry Letters*, 71–74.

Ogawa, M., Hashizume, T., Kuroda, K. and Kato, C. (1991) Intercalation of 2,2′-bipyridine and complex formation in the interlayer space of montmorillonite by solid-solid reactions. *Inorganic Chemistry*, **30**, 584–585.

Ogawa, M., Takahashi, M., Kato, C. and Kuroda, K. (1994) Oriented microporous film of tetramethylammonium pillared saponite. *Journal of Materials Chemistry*, **4**, 519–523.

Ogawa, M., Kadomoto, H., Kato, C. and Kuroda, K. (1997) Intercalation of a crown-ether into layered silicates. *Clay Science*, **10**, 185–194.

Ozin, G.A. (1989) Advanced zeolite materials science. *Angewandte Chemie International Edition in English*, **28**, 359–376.

Papadimitrakopoulos, F., Zhang, X.-M., Thomsen III, D.L. and Higginson, K.A. (1996) A chemical failure mechanism for aluminum(III) 8-hydroxyquinoline light-emitting devices. *Chemistry of Materials*, **8**, 1363–1365.

Patil, O., Curtin, D.Y. and Paul, I.C. (1984) Solid-state formation of quinhydrones from their components. Use of solid-solid reactions to prepare compounds not accessible from solution. *Journal of American Chemical Society*, **106**, 348–353.

Rastogi, R.P., Singh, N.B. and Singh, R.P. (1977) Organic solid-state reactions. *Journal of Solid State Chemistry*, **20**, 191–200.

Sheats, J.R., Antoniadis, H., Hueschen, M., Leonard, W., Miller, J., Moon, R., Roitman, D. and Stocking, A. (1996) Organic electroluminescent devices. *Science*, **273**, 884–888.

Sugahara, Y., Kuroda, K. and Kato, C. (1984) Synthesis β-sialon from a montmorillonite-polyacrylonitrile intercalation compound by carbothermal reduction. *Journal of the American Ceramic Society*, **67**, C247–C248.

Tang, C.W. and Van Slyke, S.A. (1987) Organic electroluminescent diodes. *Journal of Applied Physics*, **51**, 913–915.

Tang, C.W., Van Slyke, S.A. and Chen, C.H. (1989) Electroluminescence of doped organic thin films. *Journal of Applied Physics*, **65**, 3610–3616.

Theng, B.K.G. (1974) *The Chemistry of Clay-Organic Reactions*. Adam Hilger, London.

https://doi.org/10.1346/000986002320514154 Published online by Cambridge University Press

Toda, F., Tanaka, K. and Sekikawa, A. (1987) Host-guest complex formation by a solid-solid reaction. *Journal of the Chemical Society, Chemical Communications*, 279–280.

Van Olphen, H. (1977) *An Introduction to Clay Colloid Chemistry*, 2nd edition. Wiley-Interscience, New York.

Van Slyke, S.A., Chen, C.H. and Tang, C.W. (1996) Organic electroluminescent devices with improved stability. *Applied Physics Letters*, **69**, 2160–2162.

Whittingham, M.S. (1982) Intercalation chemistry: an introduction. Pp. 1–18 in: *Intercalation Chemistry*. (M.S. Whittingham and A.J. Jacobson, editors) Academic Press, New York.

Yariv, S. (1990) Combined DTA-Mass spectrometry of organo-clay complexes. *Journal of Thermal Analysis*, **36**, 1953–1961.

Yariv, S. (1991) Differential thermal analysis (DTA) of organo-clay complexes in thermal analysis in the geosciences. Pp. 328–351 in: *Lecture Notes in Earth Sciences,* **38** (W. Smykatz-Kloss and S. St.J. Warne, editors). Springer Verlag, Berlin.

Zhang, L.G., Ren, X.G., Jiang, D.P., Lu, A.D. and Yuan, J.S. (1996) Effect of metal cation on absorption and fluorescence spectra of metal complexes of 8-hydroxyquinoline. *Spectroscopy Letters*, **29**, 995–1001.

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