Notes

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m), 3.39 (1H, d, $J=13.3$), 3.54 (1H, dd, $J=13.3$, 2.8), 5.14 (1H, quin, $J=3.6$), 7.75 (1H, bs); δ_C (CDCl$_3$) 21.5, 25.4, 27.5, 46.2, 65.9, 170.8, 172.3. (Found: C, 53.6; H, 7.11, N, 8.89. Calc. for C$_7$H$_{11}$NO$_3$: C, 53.5; H, 7.05, N, 8.91%).

γ-(Acetyloxy)methyl-γ-butyrolactone **dl-5**. -Silver acetate (167 mg, 1.0 mmol) was added to γ-iodo- (**1b**) or γ-chloromethyl-γ-butyrolactone (**1c**) (0.2 mmol) obtained from PPL-mediated resolution in acetic acid (10 mL) and stirred at room temperature under N$_2$ atmosphere. After 1 hour no starting material was left on TLC. CH$_2$Cl$_2$ (100 mL) was added and the solution was washed with brine three times to remove acetic acid. The organic layer was dried over anhydrous MgSO$_4$, filtered and concentrated under reduced pressure to give crude product. Purification by flash chromatography gave colorless oily product (**3**) in 86 and 79% yield from γ-iodo- or γ-chloromethyl-γ-butyrolactone respectively. δ_H (CDCl$_3$; J/Hz) 1.91-2.07 (1H, m), 2.18 (3H, s), 2.24-2.46 (1H, m), 2.52-2.63 (2H, m), 4.13 (1H, dd, $J=10.4$, 6.2), 4.31 (1H, dd, $J=10.4$, 3.8), 4.63-4.80 (1H, m); δ_C (CDCl$_3$) 20.5, 23.7, 28.0, 65.2, 77.1, 170.6, 176.6.

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Synthesis of Intercalation Compounds between a Layered Double Hydroxide and an Anionic Dye

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Introduction

Layered double hydroxides (LDHs) are minerals and synthetic materials with positively charged brucite-type layers of mixed-metal hydroxides. Exchangeable anions located in the interlayer spaces compensate for the positive charge of the brucite-type layers. The chemical composition of the LDH is generally expressed as $[M^{2+}{}_{1-x}M^{3+}{}_x(OH)_2]^{x+}[(A^{n-})_{x/n} H_2O]^{x-}$ with $x=[M^{3+}]/([M^{2+}]+[M^{3+}])$. Here, $M^{2+}=Mg^{2+}$, Co^{2+}, Ni^{2+}, etc., $M^{3+}=Al^{3+}$, Cr^{3+}, etc., and A^{n-} is an interlayer exchangeable anion such as $CO_3{}^{2-}$, Cl$^-$, etc. These ionic layered materials also have been termed "hydrotalcite-like" compounds in the reference to the structural similarity to the mineral hydrotalcite, $[Mg_6Al_2(OH)_{16}][CO_3]\cdot4H_2O$, or termed "anionic clays" in mirror image resemblance to the cationic clays whose negative charge of the aluminosilicate layers are counterbalanced by the intercalated cations. The preparations, properties, and applications of LDH materials have been studied extensively.[1~7] They are used as adsorbents, catalysts, catalyst precursors, aninoic exchangers, and antacid drugs.[8~11]

There have been several reports on the intercalation of organic anions into the LDH.[12,13] The main synthetic route has been performed by anionic exchange. Among the various organic substances used as the interlayer guest species, dyes are one of the most interesting materials because their host-guest interaction may provide unique structural features and physicochemical properties. Intercalation compounds between a LDH and an anionic dye are expected to have several

uses such as in pigments and in the recovery of anionic dyes from waste water. LDHs of aluminium with magnesium intercalated with naphthol yellow S, indigo carmine, and new coccine as anionic dyes have been reported so far.[14,15] In this study, intercalation of an indigo carmine and a potassium indigotetrasulfonate into the LDH of aluminium with zinc were attempted by using direct synthesis.

Experimental

The layered double hydroxide of aluminium with zinc (Zn-Al LDH) was synthesized by hydrolysis of the mixed aqueous solutions of $ZnCl_2$ (1.5 mol dm^{-3}), $AlCl_3$ (0.5 mol dm^{-3}) at pH = 7.5±0.2 by dropwise addition of an aqueous NaOH solution (1.0 mol dm^{-3}) with vigorous stirring under a nitrogen atmosphere. The molar ratio of aluminium is 0.25. The precipitate was aged at 60 ℃ for 24 hours, filtrated, washed with decarboxylated water, and air dried at 80 ℃ for 18 hours. Intercalation compound of an indigo carmine into the LDH of aluminium with zinc (Zn-Al-IC LDH) was directly synthesized by hydrolysis of the mixed aqueous solutions of $ZnCl_2$ (0.075 mol dm^{-3}), $AlCl_3$ (0.025 mol dm^{-3}), and an indigo carmine (0.025 mol dm^{-3}) at pH = 7.5±0.2 by dropwise addition of an aqueous NaOH solution (1.0 mol dm^{-3}) with vigorous stirring under a nitrogen atmosphere. The amount of indigo carmine, which form two anions, corresponded to about two equivalents of the stoichiometric interlayer anions calculated from the aluminium contents. The precipitate was aged at 70 ℃ for 7 days, filtrated, washed with decarboxylated water, and air dried at 80 ℃ for 18 hours. Intercalation compound of a potassium indigotetrasulfonate into the LDH of Al and Zn (Zn-Al-PI LDH) was synthesized by a similar method to Zn-Al-IC LDH. Indigo carmine and potassium indigotetrasulfonate were obtained from Sigma and used without further purification.

Chemical analysis for Zn and Al was carried out by using an inductively coupled plasma emission spectrometer (ARL Model 3410 ICP-AES). The dye content of the product was determined using an Vario EL CHN analyzer. Infrared spectra were recorded on a Midac Prospect FT-IR spectrometer. X-ray diffraction spectrum was obtained with a Rigaku diffractometer using Cu-K_α radiation.

Results and Discussion

Indigo Carmine

Potassium indigotetrasulfonate
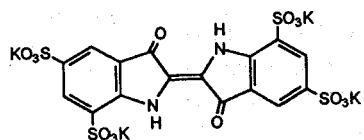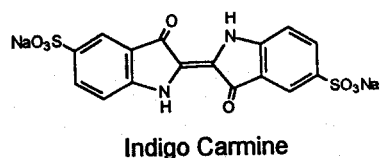
Scheme 1.

Layered double hydroxide of Al and Zn (Zn-Al LDH) was directly synthesized by the hydrolysis of $ZnCl_2$, and $AlCl_3$, with a NaOH solution. The interlayer anion is Cl^-. Intercalation compound between an indigo carmine and a layered double hydroxide of Al and Zn (Zn-Al-IC LDH) was directly synthesized by the hydrolysis of $ZnCl_2$, $AlCl_3$, and the indigo carmine with a NaOH solution. Intercalation compound of a potassium indigotetrasulfonate into the LDH of aluminium with zinc (Zn-Al-PI LDH) was synthesized by a similar method to Zn-Al-IC LDH. Figure 1 show the X-ray diffraction patterns of Zn-Al LDH, Zn-Al-IC LDH, and Zn-Al-PI LDH. Top panel shows the X-ray diffraction patterns of the Zn-Al LDH. The indexing of the diffraction peaks was obtained by comparison with the diagram reported for Mg-Al LDH.[7] The a parameter of the hexagonal cell unit corresponds to the distance between two metal cations in adjacent octahedra while the c parameter corresponds three times the distance between adjacent hydroxyl layers. The c-axis parameter was calculated to be 23.44 Å from averaging of the positions (003) and (006) peaks. The a-axis parameter was calculated to be 3.084 Å from the position (110) peak. The basal spacing of the Zn-Al LDH is 7.81 Å. The gallery height of Zn-Al LDH is 3.01 Å when the thickness of the $Zn(OH)_2$ layers (4.80 Å) is substracted.[16]

Middle panel shows the X-ray diffraction patterns of the Zn-Al-IC LDH. The (003) diffraction peak and the higher order peaks of the Zn-Al-IC LDH shifted to lower 2θ angles compared to those of the Zn-Al LDH. The c-axis parameter of the Zn-Al-IC LDH was calculated to be 67.3 Å from averaging of the positions (003) and (006) peaks. The basal spacing of the Zn-Al-IC LDH increased to 22.43 Å from 7.81 Å of the Zn-Al LDH. Therefore, the gallery height of the Zn-Al-IC LDH was 17.63 Å. This increase in the gallery height
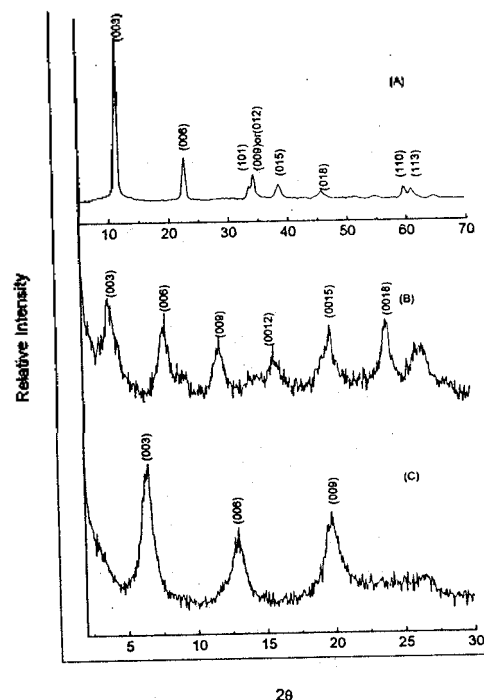

Figure 1. X-ray diffraction patterns and Miller indices of (A) Zn-Al LDH, (B) Zn-Al-IC LDH, and (C) Zn-Al-PI LDH.

strongly indicated the intercalation of the indigo carmine into the Zn-Al LDH. Bottom panel shows the X-ray diffraction patterns of the Zn-Al-PI LDH. The (003) diffraction peak and the higher order peaks of the Zn-Al-PI LDH shifted to lower 2θ angles compared to those of the Zn-Al LDH. However, the (003) diffraction peak and the higher order peaks of the Zn-Al-PI LDH shifted to higher 2θ angles compared to those of the Zn-Al-IC LDH. The c-axis parameter of the Zn-Al-PI LDH was calculated to be 40.35 Å. The basal spacing of the Zn-Al-PI LDH increased to 13.45 Å from 7.81 Å of the Zn-Al LDH. Therefore, the gallery height of the Zn-Al-PI LDH was 8.65 Å. This increase in the gallery height also indicated the intercalation of the potassium indigotetra- sulfonate into the LDH. The infrared spectra of the intercalation compounds were similar to those of the solid state dye salts in the range of 1700-1000 cm^{-1}. These indicated also that the indigo carmine and the potassium indigotetra- sulfonate were intercalated into the Zn-Al LDH, respectively.

The formula of the Zn-Al-IC LDH was checked by ICP-AES and C, H, N, S elemental analysis. From chemical analysis, the formula of the compound synthesized can be written as $[Zn_{0.75}Al_{0.25}(OH)_2][(IC)_{0.10} \cdot mH_2O]$. Since the indigo carmine have two anions, the ideal formula of the Zn-Al-IC LDH can be expressed as $[Zn_{0.75}Al_{0.25}(OH)_2][(IC)_{0.125} \cdot mH_2O]$. The contents of the intercalated indigo carmine was estimated to be about 80% of the ideally calculated contents. Therefore, the formula of the synthesized Zn-Al-IC LDH rather can be written as $[Zn_{0.75}Al_{0.25}(OH)_2][(IC)_{0.10} (Cl^-)_{0.05} \cdot mH_2O]$. The unreacted Zn-Al LDH was not detected by the X-ray diffraction analysis. We confirmed that the unreacted Cl$^-$ contents did not affect the basal spacing. The contents of indigo carmine corresponded to about half of the stoichiometric aluminium contents of LDH. This fact indicates that one of two sulfonate groups of the indigo carmine attach with positively charged upper hydroxide layer, the other sulfonate group attach with another positively charged lower hyrdoxide layer. By taking into account the molecular size and rigid shape of the indigo carmine, the unreacted Cl$^-$ and H$_2$O were inserted into the interlayer site of the pillared indigo carmine with LDH. The formula of Zn-Al-PI LDH, $[Zn_{0.74}Al_{0.26}(OH)_2][(PI)_{0.02} (Cl^-)_{0.18} \cdot mH_2O]$, was checked by a similar method to Zn-Al-IC LDH. Since the potassium indigotetrasulfo- nte have four anions, the contents of the intercalated potassium indigotetrasulfonte was estimated to be only about 32% of the ideally calculated contents. However, the unreacted Zn-Al LDH was not detected by the X-ray diffraction analysis.

From X-ray diffraction studies, the orientation of the intercalated species can be roughly estimated. The size of the indigo carmine was calculated by using Alchemy program. The length between two sulfonate groups of the indigo carmine is 16.9 Å, when the van der Waals radius of oxygen is to assumed to be 1.40 Å.[17] The gallery height of the Zn-Al-IC LDH measured from the X-ray diffraction peaks is 17.63 Å. The estimated length of the indigo carmine is slightly less than the gallery height. Therefore, the molecular plane of the indigo carmine and its C=C axis lie perpendicular to the hydroxide layers. This geometric orientation result is equal to that of the intercation of the indigo carmine into LDH of aluminium with magnesium (Mg-Al-IC LDH).[14]

The gallery height of the Mg-Al-IC LDH measured from the X-ray diffraction peaks is 17.4 Å. Kato *et al.* suggested that the indigo carmine anions are arranged with their C=C axes nearly perpendicular to the hydroxide layers. Therefore, the interaction of the indigo carmine with the Zn-Al LDH is equal to that with the Mg-Al LDH. This indicates that the host LDH species does not play a role in the intercalation of the indigo carmine into the LDH.

The size of the potassium indigotetrasulfonate was also calculated in a similar manner. The length between two sulfonate groups of the potassium indigotetrasulfonate is 14.3 Å, and the width of the potassium indigotetrasulfonate molecular plane is 8.9 Å. The gallery height of the Zn-Al-PI LDH measured from the X-ray diffraction peaks is 8.65 Å. The gallery height is approximately equal to the width of the potassium indigotetrasulfonate. We expect that two of four sulfonate groups of the potassium indigotetrasulfonate attach with positively charged upper hydroxide layer, other two sulfonate groups attach with another positively charged lower hydroxide layer. Therefore, the molecular plane of the potassium indigotetrasulfonate is oriented perpendicular to the hydroxide layers, while its C=C axis is arranged parallel to the hydroxide layers. However, the intercalated potassium indigotetrasulfonate was estimated only about 32% of the ideally calculated contents. The more complete characterization of orientation of the potassium indigotetrasulfonate with different contents is under investigation. Schematic illustration of the arrangement of the indigo carmine and the potassium indigotetrasulfonate in the Zn-Al LDH are shown in Figure 2.

In conclusion, we synthesized intercalation compounds of an indigo carmine and a potassium indigotetrasulfonate into the LDH of aluminium with zinc. From the X-ray diffraction data, the orientation of the intercalated indigo carmine and
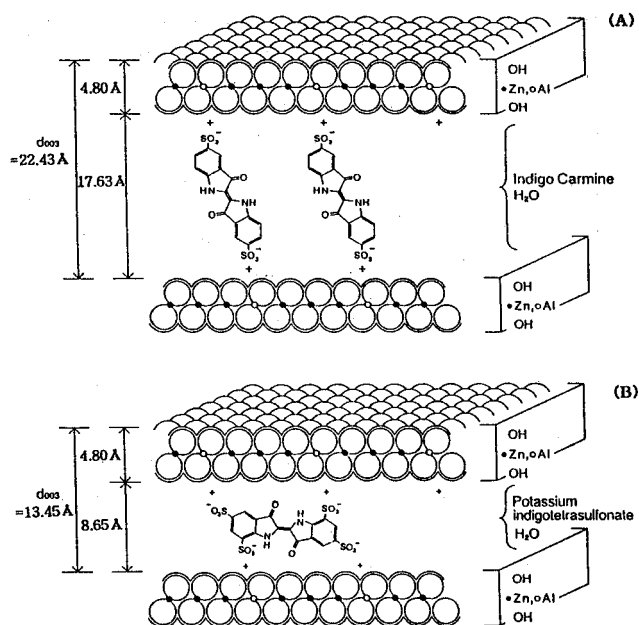

Figure 2. Schematic illustration of the orientation of (A) indigo carmine and (B) potassium indigotetrasulfonate intercalated in the Zn-Al LDH.

potassium indigotetrasulfonate into the Zn-Al LDH were determined. For the indigo carmine, the molecular plane of the indigo carmine and its C=C axis lie nearly perpendicular to the hydroxide layers. However, the molecular plane of the potassium indigotetrasulfonate is orinted perpendicular to the hydroxide layers, while its C=C axis is arranged parallel to the hydroxide layers. Therefore, the guest species play an important role in the intercalation of guest species into the Zn-Al LDH.

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Bispsoralen Derivatives Linked with a Polymethylene Bridge Containing a Hydroquinone Moiety

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Psoralens are widely used as dermal photosensitizing agents for the treatment of various skin diseases,[1-4] e.g., vitiligo, psoriasis, mycosis fungoides, chronic leukemia, and some infections connected with AIDS[5] and as chemical tools for the study of nucleic acid structure-function relationship.[6,7] A large number of studies on the mechanism of the photochemical reactions between psoralen and DNA bases *in vivo*[8] or with thymine derivatives[9,10] have been carried out. These studies involved intermolecular processes leading generally to a mixture of several photoproducts. Binding of psoralens to DNA is generally the consequence of two successive events: (a) intercalation of the psoralen between the base pairs of nucleic acids in the ground state;[11,12] (b) photo [2+2]conjugation of the complexed psoralen to pyrimidine bases of DNA between the pyrimidine 5,6 double bond and 3,4 and/or 4′,5′ double bond of the psoralen molecule.[8,13] The formation of the intercalated complex between psoralens and DNA is an important step which markedly affects the successive covalent photobinding to the macromolecule. In order to gain insight into these two processes in the absence of complicating factors associated with hydrogen bonding or the usual carbohydrate and phosphodiester linkages, Lhomme and Decout[14] prepared a series of model compounds **3** and showed that the polymethylene bridges allow intramolecular ring-ring stacking between the two aromatic units with possible superposition of the double bonds. Castellan *et al.*[15] also investigated the interactions and the photoreactions of synthetic derivatives of psoralen containing the psoralen and the thymine rings, the two psoralen rings (**4**), or the two thymine rings. The reactivity of the bispsoralen **4** were reported to be sensitive to the presence of cations because the cation added made the conformation of the polyoxyethylene chain folded, increasing the intramolecular interaction between two psora-
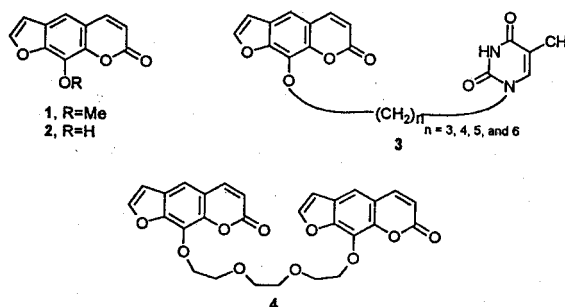

Figure 1. Chemical Structures of 8-MOP (1), 8-hydroxypsoralen (2) and psoralen analogues (3, 4).