BENZOPHENONE-SENSITIZED CYCLODIMERIZATION OF CINNAMIC ACID IN HYDROTALCITE INTERLAYERS: A STUDY OF THE SENSITIZATION BEHAVIOR

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ABSTRACT

Aromatic ketone-sensitized cyclodimerization was studied in the presence of an anion exchange, clay, hydrotalcite. UV irradiation of the clay suspension coadsorbing trans-cinnamate and 4-benzoylbenzoate ions resulted in the efficient formation of a syn-head-to-head dimer. The ratio of the cis/dimer was significantly affected by the introduction of heavy atom substituents of the sensitizers in high concentrations but not in lower concentrations. Dimerization was revealed to be 10 times more efficient than $E-Z$ isomerization by extrapolating to infinitely smaller concentrations of the sensitizers. The sensitization mechanism through the formation of an exciplex between the excited singlet 4-benzoylbenzoate and trans-cinnamate is presented on the basis of the efficient formation and stereoselectivity of the cyclodimer. A fluorescent probe, the 2-naphthoate ion, intercalated in the clay interlayers was shown to increase its fluorescence intensity in the presence of a sensitizer, implying the validity of a singlet sensitization mechanism via an exciplex formation. The turnover number for the energy transfer exceeded 40 per sensitizer molecule, thus the cyclodimerization was found to proceed catalytically with the sensitizers.

Key words: Intercalation, Hydrotalcite, Cinnamic acid, Sensitized cyclodimerization, Stereochemistry

INTRODUCTION

In recent years, various inorganic layered materials such as metal chalcogenides, metal halides, alumino silicates (clay minerals) and zirconium phosphate have been applied as host compounds for the aggregation of photofunctionalized organic molecules in their interlayer spaces. The incorporation of organic molecules are achieved using various methods: Ion exchange, ligand exchange, and the covalent bond formation between an adsorbate and an inorganic layer, just to name a few, while a wide variety of molecular aggregates have been observed. Photochemical reactions utilizing such molecular aggregations as incorporated compounds are significant in terms of synthetic applications, i.e., for the capacity to change the reaction courses as well as the control of the stereoselectivities of the photoproducts.

Previously, we have reported on the photoinduced cyclodimerization of ionic olefins...
intercalated in the interlayers of clay minerals.\textsuperscript{10,11} Photoirradiation of stilbene-4-carboxylate ions (stb\textsuperscript{-}) resulted in the efficient formation of syn-head-to-head and syn-head-to-tail cyclodimers in the presence of hydrotalcite clay.\textsuperscript{11} Such efficient formations and stereoselectivities of the photodimers could be reasonably explained by the well-organized molecular aggregation in the clay interlayers in which the stb\textsuperscript{-} ions are packed in antiparallel orientation.

The present article explains the benzophenone-sensitized photocyclodimerization of cinnamate ions intercalated in hydrotalcite clay interlayers. Although benzophenone has a large intersystem crossing rate ($k_{\text{isc}} \approx 10^{12} \text{ s}^{-1}$) and is well known as a typical triplet sensitizer, its excited singlet state has also been shown to play an important role in condensed reaction systems.\textsuperscript{12} In this study, we deal with the possibility of an unusual singlet sensitization of benzophenone derivatives (1) incorporated in clay interlayers by a probe of the photocyclodimerization reaction of cinnamic acids (2) and a fluorescence spectroscopy study using 2-naphthoic acid (3).
RESULTS AND DISCUSSION

Figure 1 shows the laminating structure of hydrotalcite clay which consists of the hydroxide layer and the gallery anion. Octahedral units of Mg(OH)$_2$ are connected to form a sheet, while these units are, in part, isomorphously replaced by Al(OH)$_2^+$, forming polycationic layers which are neutralized by the presence of anions in its interlayers. The gallery anion can be exchanged by various other anions, even by organic species such as carboxylate, sulfonates and phosphonates. Alcamac Cl, the hydrotalcite clay employed in this study, was manufactured by Kyowa Chemical Ltd, in which about 1/3 of the Mg$^{2+}$ was replaced with the Al$^{3+}$ and Cl$^-$ ions present in the interlayers.

**Intercalation of guest molecules**

The intercalation of the guest aromatic ketones (1) and olefins (2) into the clay interlayers was carried out by adding an appropriate amount of powdered hydrotalcite into an aqueous solution of a mixture of the sodium salts of 1 and 2. The intercalation degrees of the carboxylates as well as the gallery heights of the intercalated compounds are summarized in Table 1. The intercalation degrees were measured by the UV adsorption spectra of the substrates remaining in the bulk solution. Intercalation did not occur quantitatively (35–80%), presumably due to the hydrophobicity of the compounds: The more hydrophobic the substrate, the larger the resulting intercalation degree. The gallery heights were calculated from the 003 basal spacings of the intercalated compounds which were obtained by means of powder X-ray diffraction analysis in which the thickness of the hydrotalcite layer (4.77 Å) was subtracted from the basal spacing. Changes in the gallery heights reasonably correspond to the molecular length of the carboxylates, thus implying that the incorporated carboxylates are adsorbed in the hydrotalcite interlayer and aggregated in monolayer fashion.

![Structure of hydrotalcite clay](image)

**FIG. 1.** Structure of hydrotalcite clay, [Mg$_{2/3}$Al$_{1/3}$OH$_2$]$_{x}$1/3•mH$_2$O; (a) an octahedral unit of Mg(OH)$_2$, and (b) layered structure of the hydroxides. 1/3 of Mg$^{2+}$ ion is isomorphously replaced by the Al$^{3+}$ ion.
TABLE 1. Intercalation degrees of carboxylates into hydrotalcite interlayers and changes in the gallery heights*

<table>
<thead>
<tr>
<th>compound</th>
<th>intercalation degreeb (%)</th>
<th>gallery heightc (Å)</th>
<th>molecular lengthd (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>63.1</td>
<td>15.0</td>
<td>11.0</td>
</tr>
<tr>
<td>1b</td>
<td>70.1</td>
<td>–</td>
<td>11.0</td>
</tr>
<tr>
<td>1c</td>
<td>78.9</td>
<td>15.6</td>
<td>11.1</td>
</tr>
<tr>
<td>1d</td>
<td>84.9</td>
<td>–</td>
<td>11.4</td>
</tr>
<tr>
<td>1e</td>
<td>80.3</td>
<td>–</td>
<td>11.6</td>
</tr>
<tr>
<td>1f</td>
<td>75.5</td>
<td>16.1</td>
<td>12.1</td>
</tr>
<tr>
<td>1g</td>
<td>77.8</td>
<td>19.3</td>
<td>15.7</td>
</tr>
<tr>
<td>2a</td>
<td>44.3</td>
<td>12.9</td>
<td>9.10</td>
</tr>
<tr>
<td>2b</td>
<td>80.9</td>
<td>13.5</td>
<td>10.9</td>
</tr>
<tr>
<td>2c</td>
<td>83.2</td>
<td>15.3</td>
<td>11.2</td>
</tr>
</tbody>
</table>

* Carboxylates (1 and 2) were intercalated from the aqueous solution of their sodium salt; [carboxylate] = [hydrotalcite] = 10 mM, 60 °C, overnight. c Intercalation degrees are values when each carboxylate is intercalated independently, which were measured from absorption spectra of filtrates. d Gallery heights were calculated from interlayer distances obtained by powder X-ray diffraction analysis.

Sensitized cyclodimerization of trans-cinnamate (2a) in hydrotalcite interlayers

Photoirradiation of an aqueous suspension of clay-intercalated compounds involving trans-cinnamate (2a) and 4-benzoylbenzoate ions (1a) with light of λ > 320 nm resulted in the formation of a cis-isomer and a syn-head-to-head dimer, β-truxinate (Table 2). This reaction was clearly initiated by the excited 1a since no reaction occurred in its absence. Only an E – Z isomerization could be observed in the uv irradiation of a solution of 1a and 2a without clay. We can see, therefore, that the hydrotalcite interlayer is an indispensable and effective medium in realizing efficient cyclodimerization reactions.

An interesting point of observation is that the same cyclodimer, syn-HH, was formed both in the case of the direct irradiation of 2a as well as with the sensitized reaction. In usual [2 + 2] photocycloadditions of aromatic olefins, syn-dimers are produced as the major isomers by way of a singlet excimer. However, photoreactions via excited triplet states
TABLE 2. Sensitized and direct irradiated cyclodimerization of cinnamate (2a) incorporated in hydrotalcite interlayers.

<table>
<thead>
<tr>
<th>concentration (mM)</th>
<th>λ (nm)</th>
<th>conversion (%)</th>
<th>selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a 2a clay</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 5 10</td>
<td>&gt;320</td>
<td>70</td>
<td>60 40</td>
</tr>
<tr>
<td>0 5 10</td>
<td>&gt;320</td>
<td>0</td>
<td>– –</td>
</tr>
<tr>
<td>5 5 0</td>
<td>&gt;320</td>
<td>50</td>
<td>100 0</td>
</tr>
<tr>
<td>0 10 10</td>
<td>&gt;280</td>
<td>92</td>
<td>53 46</td>
</tr>
</tbody>
</table>

* Products were analyzed by GLC. b Conversions are based on trans-2a.

usually cause an $E - Z$ isomerization reaction and/or significant formations of anti-dimers. Indeed, all of the reactions were of $E - Z$ isomerization and no dimerization occurred at all in sensitization reactions without clay. The fact that only the syn-HH dimer was efficiently formed in spite of the use of a triplet sensitizer can be interpreted in two ways, i.e., an unusual stereochemical control by spatial restriction and/or a singlet sensitization mechanism by way of an exciplex formation. Analysis by spatial restriction can be explained as follows: Upon photoexcitation, 1a rapidly converts into its excited triplet state followed by an energy transfer from the triplet 1a to 2a. The triplet 2a thus formed undergoes an $E - Z$ isomerization observed in usual photoreaction systems. However, the reaction course changes to that for cyclodimerization under conditions in which the olefin molecules become highly packed as aggregates in the interlayer spacings of the hydrotalcite clay.

The other possibility that can be considered for the formation of a cyclodimer may be the singlet sensitization process between the excited singlet 1a and 2a, although it should be noted that such sensitization does not take place in solution. The energy transfer or complexation between the excited singlet 1a and 2a occurs before the intersystem crossing to the triplet state. In such cases, photodimerization is induced by the excited singlet sensitizer in a manner similar to that in direct photoreactions. 1a with a benzoyl moiety has a very fast intersystem crossing rate of at least $10^{12}$ s$^{-1}$ and acts exclusively as a triplet sensitizer, its triplet lifetime being $10^{-6}$ s$^{-1}$. In spite of the facile population of the excited triplet states, judging from the fact that the ionic molecules are highly condensed and stacked in regulated monolayer aggregation, this sensitization in the clay interlayers occurs in the singlet state prior to intersystem crossing.

Triplet exciplex intermediates have been identified in the photoreaction of benzo-phenone with electron rich olefins. In the present reaction, however, the passway through the triplet exciplex can not be applied for the sensitized cycloaddition, judging from the fact that no cyclodimer was formed in the solution. If the cycloaddition took place by way of a triplet exciplex, excited triplet state of 1a could be quenched by 2a to form a triplet exciplex within its sufficient long lifetime ($10^{-6}$ s$^{-1}$) giving the cyclodimer even in a rather lower concentration of 2a. The absence of the cyclodimer product in solution seems to neglect the possibility of the triplet exciplex passway.
Heavy atom effect

As mentioned above, the syn-HH dimer and cis isomer can reasonably be assumed to be produced from the singlet or triplet sensitizations, respectively, by using la as the sensitizer. The distribution of these products is significantly affected by the heavy atoms substituted on the sensitizer since the intersystem crossing of la and the singlet energy transfer between la and 2a are expected to compete with each other. Thus, changes in the product cis/dimer ratio was investigated using p-substituted benzoylbenzoic acids.

Figure 2 shows the plots of the cis/dimer ratio against the concentration of the sensitizers. The product distribution was studied in its initial stage by constant uv irradiation for 10 min. The effects of the substituent on the cis/dimer ratio were found to be extremely sensitive to the concentration of the sensitizers as the ratios were observed to vary with the change in their concentrations. When concentrations of the sensitizers were high, a significant difference in the cis/dimer ratio could be observed among the sensitizers, suggesting an acceleration of the intersystem crossing by the heavy atom substituents of the sensitizers. In the case of aryloylbenzoate, the yields of the cis isomer increased with the increase in the atomic weight of the substituent of the sensitizers (ld-f) and (aryloylphenyl) benzoate lg. These results clearly support the occurrence of a singlet energy transfer to 2 or an exciplex formation competing with the intersystem crossing forming a triplet excited 1.

![Figure 2. Heavy atom substituents and concentration effects of sensitizers on the photocyclodimerization reaction of trans-cinnamate (2a) incorporated in hydrotalcite interlayers; open circle la, filled circle lb, open square lc, filled square ld, open triangle le, filled triangle lf, dotted circle lg; [1+2a]=[clay]=5 mM, irradiation; >320 nm, 10 min.](image)
In low concentrations, however, little substituent effect of the sensitizers could be observed. In the plots of the cis/dimer ratio against the concentration of the sensitizers, extrapolation of the [sensitizer] to 0% resulted in a cis/dimer ratio of ca. 0.1 for every sensitizer. The cis/dimer ratio shows the singlet energy transfer to be 10 times as fast as the intersystem crossing of 1a, assuming that the dimers and the cis isomers are formed from the excited singlet and triplet states, respectively. Such energy transfers cannot compete with the intersystem crossing of 1a because of the very fast rate constant, $k_{isc} = 10^{12} \text{s}^{-1}$, since the singlet excitation energy of 1a is 15 kcal/mol lower than that of 2a. Therefore, it can be proposed that the sensitized cyclodimerization proceeds through the exciplex formation between the excited singlet 1 and the ground state 2a. That is, an excited benzophenone interacts with the adjacent cinnamate to generate an exciplex followed by the formation of an excimer of the cinnamate which thus leads to cyclodimerization.

**Substituent effect**

Sensitized cyclodimerizations of clay-intercalated p-cyano and p-methoxy cinnamic acids (2b and 2c) were investigated in order to clarify the formation of the exciplex which is believed to act as an intermediate. Figure 3 shows the plots of the product ratios vs the irradiation time in the uv irradiation of clay inclusion samples of 2 together with 5% of 1a as the sensitizer. Syn-HH cyclodimers were formed, similar to the case of 2a. The ratios of the cis isomer and the cyclodimer were almost constant in every irradiation time interval: cis/dimer = 0.25 and 0.65 for 2b (p-cyano) an 2c (p-methoxy), respectively. Excited benzophenone and its derivatives have been reported to sensitize E-Z isomerization and the oxetane formation of olefins.\(^\text{15}\) It has been established that an exciplex formed by the interaction of an excited ketone with an olefin is responsible for the photoreactions.\(^\text{16}\) Similarly, it is believed that the present endothermic sensitization proceeds through a pathway of exciplex formation for the cyclodimerization of cinnamate ions in clay, as illustrated in the following scheme.

\[
\begin{align*}
&\begin{array}{c}
\text{1a} \\
\text{CO}_2^- \quad \text{CO}_2^-
\end{array}
\quad + \\
\begin{array}{c}
\text{2a} \\
\text{Ph} \quad \text{Ph}
\end{array}
\quad \rightarrow \quad \begin{array}{c}
\text{exciplex} \\
\text{cis-cinnamate}
\end{array}
\end{align*}
\]

**Diffuse reflectance UV absorption spectra of clay-intercalated carboxylates**

The intermolecular interaction between 1a and 2a in the ground state was investigated by diffuse reflectance absorption spectra. Figure 4 shows the absorption spectra of clay-
Fig. 3. Sensitized cyclodimerizations of (A) p-cyanocinnamate (2d) and (B) p-methoxycinnamate (2c); [1a] = 0.5 mM, [2] = 9.5 mM, [clay] = 10 mM, >350 nm, 10 min., under Ar atmosphere; closed circle trans-2, open circle cis-2, and open square syn-HH dimer.
intercalated *trans*-cinnamate (2a) and 4-benzoylbenzoate (1a) compared with mixtures of 1a and 2a. The absorption spectrum of clay-intercalated 2a shows an absorption maximum at around 270 nm with an edge at 320 nm (Figure 4a). The corresponding results observed for both clay and aqueous solutions revealed that 2a shows no intermolecular interaction in the clay interlayers. However, in the spectrum of 4-benzoylbenzoate (1a), a significant difference could be observed between the intercalated compound and solution (Figure 4b). The intensity of the absorption band at around 350 nm assigned to the \(n-\pi^*\) transition increased sharply by intercalation into the clay interlayers, presumably due to the hydrophobic conditions. That is, the intercalated guest molecules in clay experience a strongly hydrophobic environment, as solvated water is driven out from the interlayers.

![Absorption spectra](image)

**Fig. 4.** (A) Absorption spectra of *trans*-cinnamate (2a) in aqueous solution (solid line) and hydrotalcite interlayer (broken line); (B) Change of absorption spectrum of clay-intercalated 4-benzoylbenzoate (1a) due to dilution with n-octanoate, the ratios of which are shown on right side of the figure; (C) Absorption spectra of co-intercalated mixtures of 1a and 2a, solid and broken lines show the observed and calculated spectra with the various ratios of the two compounds, respectively.
Indeed, a similar spectral change is also observed by their coadsorption with octanoic acid. The absorption spectra of the co-intercalated 1a and 2a showed a good correspondence to the sum of the two spectra independent of 1a and 2a. The results indicate that no electronic interaction of 1a exists in the ground state of 2a within the interlayer space.

**Sensitized excimer fluorescence spectra of clay-intercalated 2-naphthoate (3)**

In the preceding section, the formation of an exciplex has been discussed between benzoylbenzoates and cinnamates in sensitized cyclodimerization reactions. Attempts to detect the exciplex (or excimer) were carried out spectroscopically by employing diffuse reflectance emission spectroscopy of the 2-naphthoate ion (3) in place of cinnamate (2a). 2-Naphthoic acid (3) was used instead of 2a as the emission probe not only due to its strong fluorescence but also because it structurally resembles 2a which emits only a weak fluorescence. The fluorescence spectra of 3 were measured by varying the ratio of 3 and octanoic acid, a photoinactive co-adsorbate. The monomer fluorescence of 3 showed a maximum at 355 nm in a lower ratio of 3 and octanoic acid, a photoactive co-adsorbate. The monomer fluorescence of 3 showed a maximum at 355 nm in a lower ratio of 3 and octanoic acid. A strong and broad excimer fluorescence appeared at 350-450 nm upon excitation of the clay intercalated sample mixed with 100% of 3 (Figure 5a) at 285 ± 1 nm.

Irradiation of the co-intercalated 10% of the sensitizers (1a and 1g) and 90% of 3 with light of 385 ± 1 nm absorbed only by the sensitizers, resulted in an increase in the excimer fluorescence in the presence of the sensitizers, clearly indicating the formation of excimers by sensitization. Particularly in the case of 1g, the fluorescence shifted to longer wavelengths, indicating the further strong interaction between the 2-naphthoate excimer and the sensitizer. These results indirectly but clearly support the involvement of the exciplex in the sensitized cyclodimerization of clay-intercalated cinnamates.

**Efficiency of the sensitized cyclodimerization reaction**

The facile diffusion of guest molecules adsorbed on inorganic surfaces has been noted in the photodimerization of clay-intercalated stilbazolium ions. It is vital to note the sensitization efficiency in clay interlayers, especially whether the diffusional movement is fast enough to compete with the deactivation of the excited sensitizer or not. Figure 6 shows the plots of the dimer yield against the irradiation time in the benzoylbenzoate-sensitized cyclodimerization of 2a in addition to the effects of temperature. Although the sensitizer exists in only 0.5% of the total amount of the adsorbates, the conversion of 2a to the cyclodimer exceeded more than 40%. These results indicate that just one sensitizer molecule is able to repeatedly excite more than 40 cinnamate molecules. Assuming that all the adsorbates are immobile and the sensitization occurs only between two adjacent molecules, the number of olefins to be sensitized should not exceed 6, since the single molecule adsorbed on the layer surface is surrounded by 6 other molecules.

This explanation seems rational in cases where the adsorbates migrate smoothly and freely around the interlayer surfaces. However, the efficiency of the dimer formation was not sensitive to temperature variation. The dimer yield did not increase even with a prolonged irradiation period of more than 7 hours. This can be understood by the assumption that the intercalated guest molecules show little motion on the surface of the clay. It also corresponds to the fact that intercalation into hydrotalcite clay requires several hours at an elevated temperature (ca. 60 °C).
In order to explain such a high turnover number (more than 40) for sensitization of the cyclodimerization, an energy migration mechanism observed in crystals of aromatic compounds and aromatic vinylpolymers can be proposed.
CONCLUSION

It was found that the 4-benzoylbenzoate-sensitization of cinnamate ions intercalated on hydrotalcite clay interlayers initiated cyclodimerization. The efficient formation and the exclusive stereoselectivity of the cyclodimer revealed that the sensitization proceeds by an exciplex formation between 4-benzoylbenzoate in the excited singlet state and cinnamate in the ground state, although the possibility of a triplet sensitization cannot be completely neglected. The effects of the concentration and heavy atom substituents of the sensitizer on the distribution of the photoproducts can be understood by analyzing the sensitization mechanism through the exciplex of the excited singlet sensitizer and the olefin. Exciplex formation is also supported by the fact that the excimer fluorescence of the 2-naphthoate ions intercalated on the clay interlayer increased and shifted slightly in the presence of the sensitizers.

EXPERIMENTAL SECTION

The ultraviolet and visible spectra were measured with a Shimadzu UV-265 spectrophotometer. The fluorescent spectra were recorded on a Hitachi 650-10 fluorescence spectrophotometer. GLC analyses were carried out with a Shimadzu GC-14B gas chromatograph using a 60 m capillary column of Silicon OV-1 (J & W Scientific DB-1). HPLC analyses were carried out with a Jasco HPLC instrument (Model 880-PU and 875-UV) using a 250 mm SIL column (Jasco Fine SIL-5) with CH2Cl2 or Et2O—n-hexane as the eluents. GPC was carried out using a preparative HPLC instrument (Japan Analytical
Industry Co., Ltd., LC-908) equipped with a JAIGEL-1H column with CHCl₃ as the eluent. ¹H-NMR spectra were measured with a Varian Gemini-200 NMR instrument. Mass spectra were recorded on a Shimadzu mass spectrometer (Model QP-5000), employing a direct inlet method (EI, 70 eV). Powder X-ray diffraction analyses were carried out with an X-ray diffractometer (Rigaku Denki) using Ni-filtered Cu-Kα radiation.

**Chemicals**

*Trans*-cinnamic acid (Nakarai), *trans*-4-methoxycinnamic acid (TCI), 4-benzoylbenzoic acid (TCI), and 2-naphthoic acid (Nakarai) were obtained commercially and recrystallized from benzene or ethanol before use. Other chemical reagents (extra pure grade) were used as provided unless otherwise noted. As sensitizers, 4'-substituted benzoylbenzoic acids (1b–f), were synthesized by the Friedel-Crafts acylation reaction of telephthalic acid monomethyl ester chloride (TCI) with corresponding benzene derivatives in the presence of AlCl₃, followed by saponification with KOH/EtOH. Recrystallization from ethanol produced white needles in each case: 4'-MeO (1b) mp. 256–261 °C, 4'-F (1c) mp. 242–245 °C, 4'-Cl (1d) mp. 268–272 °C, 4'-Br (1e) mp. 283–285 °C and 4'-I (1f) mp. >305 °C. 4-(4'-Benzoylphenyl) benzoic acid (1g) was also synthesized by the acylation of benzylic chloride and methyl 4-phenylbenzoate: mp. 300–304 °C. 4-Cyanocinnamic acid was synthesized by the Konoe-Vegenal reaction of malonic acid and 4-cyanobenzaldehyde in the presence of piperidine as the catalyst: mp. 272–276 °C.

Hydrotalcite clay, Alcamac™ Cl, kindly provided by Kyowa Chemicals Ltd., consisted of aluminum and magnesium hydroxides with Cl⁻ ions in the interlayers: [Mg₄.₅Al₂(OH)₁₃]Cl₂·4H₂O, the anion exchange capacity of which is 350 meq./100 g.

**Intercalation**

Excess amounts of hydrotalcite clay powder (30 mg) was added to an aqueous solution of sodium carboxylates (10 mM, 10 mL) in Pyrex tube and stirred overnight at 70 °C. After cooling, the suspension was used for photoirradiation as prepared. In order to obtain powder samples, clay-intercalated compounds were passed through a membrane filter (Advantec celluloseacetate pore size 0.45 μm) and dried in vacuo for several hours. The intercalation degrees of the compounds were estimated by means of absorption spectroscopy of the filtrate.

**Sensitized photoreaction of trans-cinnamate**

An aqueous suspension of intercalated clay powder was purged by Ar gas for 30 minutes and then irradiated with a 300 W medium pressure mercury lamp. A naphthalene solution dissolved in isooctane (>320 nm) was used as a cut-off filter. The clay layer was decomposed by adding conc. HCl and the photoproducts were extracted with CH₂Cl₂-Et₂O (2:1). After methylation with CH₃N₂, the photoproducts were analyzed by GLC in comparison with those of the authentic samples. For experiments of the concentration effects of the sensitizers (Figure 2), the photo-irradiated suspensions were filtered and the photoproducts found only in the clay-interlayers were analyzed.
Photoreaction of p-cyano and p-methoxy substituted cinnamate

The intercalation and photoreaction of p-cyano (2b) and p-methoxycinnamic acids (2c) were carried out in a similar way for 2a. An aqueous solution of 8M KNO₃ was used to pass a light over higher wavelengths (>350 nm). The photoproducts were extracted with CH₂Cl₂ under acidic conditions, then methylated with CH₂N₂. The cyclodimers were isolated using GPC (Japan Analytical Industry, LC-908) and characterized based on ¹H-NMR and mass spectra: syn-HH dimer of 2b ¹H-NMR (δ), methyl protons of methyl ester (3.78 ppm, s, 6H), cyclobutane methine protons (3.84 ppm, q, 2H, J = -2.2 Hz, 3.8 Hz, 4.50 ppm, q, 2H, J = -2.2 Hz, 3.8 Hz), aromatic protons (7.03 ppm d, 4H, J = 8.4 Hz, 7.45 ppm d, 4H, J = 8.4 Hz), mass, m/z (relative intensity), 343 (2.3), 314 (1.8), 255 (7.8), 230 (1.0), 227 (2.3), 187 (100), 156 (93), 128 (28): syn-HH dimer of 2c ¹H-NMR (δ), methoxy methyl protons (3.71 ppm, s, 6H), methyl protons of methyl ester (3.74 ppm, s, 6H), cyclobutane methine protons (3.78 ppm, q, 2H, J = 3.8 Hz, -2.2 Hz, 4.30 ppm, q, 2H, J = 3.8 Hz, -2.2 Hz), aromatic protons (6.67 ppm, q, 2H, J = 8.8 Hz, 6.84 ppm, q, 2H, J = 8.8 Hz), mass, m/z (relative intensity), 384 (0.5), 353 (1.1), 240 (1.8), 192 (100), 161 (38), 133 (8.2). Product analysis was carried out by HPLC using a Jasco Fine SIL column using ether-hexane as the eluent.

UV absorption spectra of clay intercalated compounds

An aqueous suspension of the guest intercalated hydrotalcite was passed through a membrane filter, washed with distilled water and then dried in vacuo for 6 hours. The white powder samples were ground in a mortar and mixed well with BaSO₄ of four times the amount of the powder. The absorption spectra were recorded on a Shimadzu UV instrument equipped with a diffuse reflectance attachment based on pure BaSO₄.

Diffuse reflectance emission spectra of clay-intercalated 2-naphthoate

Hydrotalcite powder was suspended in an aqueous solution of 9 mM sodium 2-naphthoate and 1 mM of the sensitizers and stirred overnight at 70 °C. The powder samples of the intercalated compounds were filtered and dried for 6 h under vacuum at room temperature. The samples were well ground and put in a quartz optical cell (10 mm x 10 mm). The quartz cell was equipped with a Hitachi fluorescence spectrometer, and the reflecting face was slanted to 60° against the incident excitation light. Emission spectra were recorded from 300 to 600 nm.

Powder X-ray diffraction analysis of guest-intercalated hydrotalcite

Changes in the gallery height were investigated by powder X-ray diffraction analyses of the inclusion compounds. Dried powder samples were used for the analysis. The 003 basal spacings of the clay layers were calculated by the Debye-Scherrer method. The gallery heights were estimated from the basal spacings by subtracting the layer thickness (4.77 Å).

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