

Dispersion and Alignment of Organic–Clay Composites within Polysilicate Thin Films by the Sol–Gel Method

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Montmorillonite clay fine particles containing alkylammonium or pyridinium guests have been observed to be highly dispersed and aligned in thin films of sol–gel polysilicate networks spin-coated on quartz slide glasses. Polarized UV and visible spectroscopic analyses of the films indicate that the organic guests are aligned not only with the interlayer surfaces of the clays but also with the sol–gel polysilicate thin films. SEM and XRD observations also confirm the anisotropic disposition of the guest molecules in the composite thin films. This is in stark contrast to the case of randomly oriented clay films prepared by the casting of the suspension on slides without any matrix.

Introduction

Clay minerals such as montmorillonite, saponite, and kaolinite have been studied in many fields as catalysts¹ and inorganic additives for the design of inorganic composite polymer materials.^{2,3} The basic structure of montmorillonite consists of octahedral aluminate layers sandwiched between tetrahedral silicate layers.^{4,5} A number of lattice-forming aluminum ions are replaced by magnesium ions to make these layers negatively charged, and they are compensated by an equivalent amount of exchangeable cations, e.g. sodium or lithium ions, within the interlayers. Cationically charged species such as organoammonium ions can be adsorbed on the clay interlayers by ion-exchange with the exchangeable alkaline cations.^{6–8} Also, the intercalated organic guest molecules can be assembled over the layer surfaces of clay particles of several micrometers.⁹ The clay interlayers are then able to provide a unique reaction space which regulates the topology of the intercalated organic molecules, inducing a remarkable stereoselectivity for photochemical reactions. As an example, we have studied the photocycloaddition of stilbazolium cations intercalated in montmorillonite interlayers.¹⁰ A syn head-to-tail cyclodimer was stereospecifically produced in montmorillonite, although the photocycloaddition occurs

in the condensed phase without clay. Furthermore, the optically functional organic molecules intercalated in the clays were found to exhibit a photochemical electron transfer in powder as well as in the suspended solution. In the case of montmorillonite intercalated with viologen dication derivatives and poly(vinylpyrrolidone) (PVP), a photoreduction of the viologen molecules was observed by UV irradiation.¹¹ The results indicate that the radical cations are quite stable in the clay interlayers, since the molecules are prevented from interacting with the oxygen atmosphere.

Our present work focuses on such organic guest–clay hybrid materials which also exhibit anisotropic properties for use in optical devices.^{12,13} We have reported here on the preparation and characterization of the thin films of polysilicate matrixes in which fine particles of montmorillonite clay ($\sim 10^{-6}$ m) including the organic guests have been dispersed. The thin films coated on the silica glass slide are interesting in that they possess the anisotropic character of the included organic guest molecules. Therefore, the present technique has great potential for applications in photofunctional devices, and the films are easy to prepare on a large-scale basis.

Experimental Procedure

(a) Synthesis of Organic–Clay Hybrid Material. Organic guest–clay hybrid materials were synthesized by ion exchange with an organic cationic species in solution. Purified standard sodium montmorillonite clay [$\text{Na}_{0.33}(\text{Al}_{1.67}\text{Mg}_{0.33})\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$] with a cation exchange capacity (CEC) of 119 mmol/100 g obtained from the Clay Science Society of Japan was used without further purification. Reagent grade 1-laurylpyridinium chloride (LPy) and *n*-octadecylamine (ODA) were obtained from the Wako Pure Chemical Industries, Ltd. and the Tokyo Kasei Pure Chemical Industries, Ltd., respectively. *p*-Methoxystilbazole (STZ) and *n*-octyl-*p*-methoxystil-

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Table 1. Maximum Wavelength of the Absorption and Emission Spectra of the Aqueous Solution of C8-STZ and STZ, and the Emission Spectra of the Organic-Clay Hybrid Powder

guest molecules	maximum wavelength (nm)	
	absorption	emission
C8-STZ	375	496 ^a
		531 ^b
STZ	368	495 ^a
		538 ^b

^a In H₂O, monomer emission. ^b In clay, excimer emission.

bazolium iodide (C8-STZ) were prepared according to previous literature.^{14,15}

A suspension of Na-montmorillonite in water (0.84 g/200 mL) was stirred magnetically overnight after adding an equivalent amount of powder organic ammonium salts at room temperature. The suspension was then passed through a membrane filter with a pore size of 0.45 μ m (Toyo Roshi Co.) to separate the clay powder involving the organic guest, washed several times with water, and dried as a powder in vacuo at room temperature. The amount of the intercalated guests was calculated from the amount dissolved in the filtrates. Finally, the dried organic guest-clay hybrid materials were ground in an agate mortar and used for experimentation.

(b) Preparation of Thin Films. Tetraethyl orthosilicate (TEOS, 4.69 g), *N,N*-dimethylformamide (DMF, 2.86 mL), absolute ethanol (4.00 mL), and a diluted aqueous solution of NH₄OH adjusted to pH = 11 (0.81 mL) were mixed in a 30 mL test tube with a molar ratio of 1.0:1.7:3.1:2.0, respectively, and stirred for 3 h at room temperature in order to hydrolyze the TEOS by sonication with an ultrasonicator (Yamato Co., type 5510). One weight percent of the organic-clay hybrid material was added to the resulting sol-gel solution. After sonication for an additional several hours, the suspension was spin-coated on a quartz glass or glass substrate at a spinning rate of 2000 rpm. The obtained thin films were kept at 60 °C overnight and dried in vacuo at room temperature for 6 h. These films are referred to as "polysilicate thin films" in this paper.

As comparison with the polysilicate thin films, a film was prepared by casting the STZ-montmorillonite hybrid particle suspension in DMF on the substrate without any matrix, then dried in vacuo at room temperature. This film is referred to as "clay film" in this paper.

(c) Characterization. X-ray analyses of the prepared samples were carried out with a RINT 2100 diffractometer (Rigaku) using Cu K α radiation operating at 40 kV and 40 mA as the applied voltage and current. The absorption and emission spectra were recorded on a JASCO V-550 and JASCO FP-750, respectively. The polarized absorption spectrum was recorded on a JASCO V-550 with a polarizer unit attachment (JASCO RSH-452). The surface and cross section of the prepared films were observed by scanning electron microscopy (SEM) with a JEOL JSM-6100 spectrometer.

Results and Discussion

(a) Properties of the Organic Guest-Clay Hybrid Material Powder. Several kinds of guest molecules, ODA, LPy, C8-STZ, and STZ, were intercalated in the montmorillonite interlayers in amounts up to the CEC. Table 1 compiles the maximum wavelengths of the absorption and emission spectra of the aqueous solutions of these organic molecules and the emission spectra of the organic-clay hybrid powders. The maximum wavelengths in the emission spectra for the hybrid powders were considerably longer than those for aque-

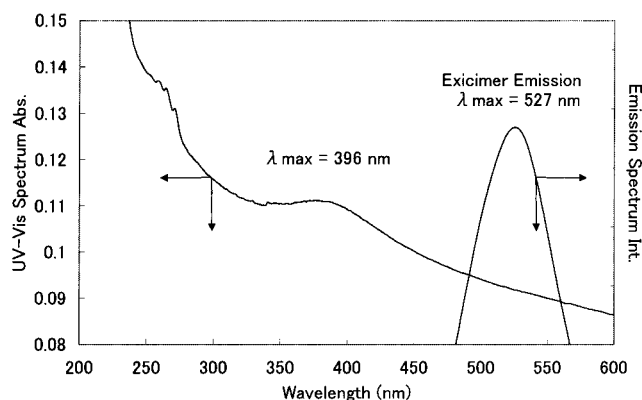


Figure 1. Absorption and emission spectra of the polysilicate thin films involving dispersed STZ-montmorillonite hybrid particles. In the emission spectrum, the excitation wavelength is 368 nm, which is the maximum wavelength of the STZ aqueous solution.

ous solutions, especially in the case of STZ, where an excimer fluorescence was observed, as has been reported.¹² This is indicative of the formation of molecular assemblies of STZ in clays which are almost perpendicularly aligned to the layer surface as monolayers.

(b) Characterization of the Polysilicate Thin Films. Figure 1 shows the absorption and fluorescence emission spectra of the polysilicate thin films containing the STZ-montmorillonite hybrid materials. A broad absorption maximum appeared at 396 nm due to the STZ molecules intercalated in the montmorillonite interlayers and dispersed throughout the films. In the fluorescence measurement of the films, the maximum was observed at 527 nm, since the excimer emission of the guest molecules is comparable in wavelength to the starting STZ-montmorillonite hybrid powder. These results revealed that the STZ molecules exist in the interlayers in an aggregated form in the montmorillonite interlayers and that they are able to stably retain their original orientation, even after the sol-gel procedures. It was confirmed that the guest molecules also maintain their optical character in the silica glass matrix throughout this sol-gel process.

(c) X-ray Diffraction of the Organic Guest-Clay Hybrid Materials. The layer distance of the clay was found to increase in accordance with the size of the organic guest molecules when these guest molecules were intercalated into the interlayers. The orientation of the guest molecules in the interlayers can be estimated from the d_{001} values, the d_{001} value of the Na-montmorillonite being 1.24 nm and the thickness of the clay silicate layer being 0.96 nm. Table 2 summarizes the layer distances of the organic guest-clay hybrid powders and those in the silica glass film by comparing their d_{001} values. The d_{001} values of the hybrid powders were seen to increase by the intercalation of these guest molecules when compared to those of Na-montmorillonite. In some cases, the d_{001} values of the organic-montmorillonite hybrid decreased during the sol-gel procedures. The STZ-montmorillonite hybrid, however, did not change its d_{001} value, even within the silica matrix, presumably because STZ has a very rigid structure compared to other organic molecules and no significant amount of the guests is able to dissolve out into the polysilicate bulk phase during the sol-gel process, while flexible guests such as C8-STZ, ODA, or

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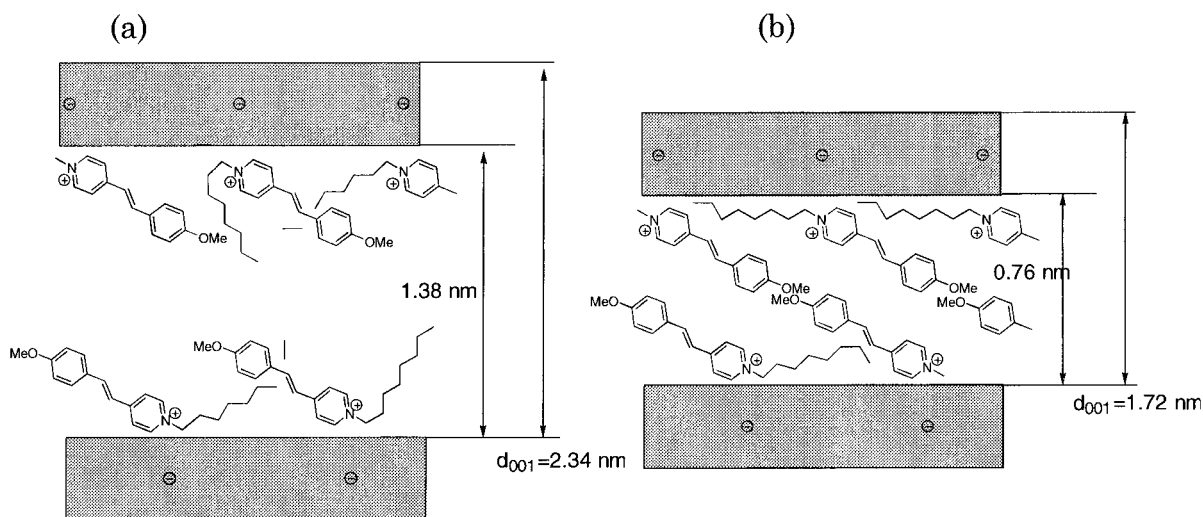


Figure 2. The orientation of the C8-STZ molecules intercalated in montmorillonite in powder (a) and in a silica matrix (b), respectively. In powder, the spaces in the clay interlayers are spread by the long alkyl chains of the organic guest molecules.

Table 2. d_{001} Values of the Na-Montmorillonite and Organic-Montmorillonite Hybrid Materials Powder and Those in the Silica Matrix

sample	d_{001} , nm (Δd_{001} , ^a nm)	
	powder	silica matrix
Na-montmorillonite	1.24 (0.28)	1.28 (0.32)
ODA-montmorillonite	1.76 (0.80)	1.32 (0.36)
LPy-montmorillonite	1.87 (0.91)	1.37 (0.41)
C8-STZ-montmorillonite	2.34 (1.38)	1.72 (0.76)
STZ-montmorillonite	1.52 (0.56)	1.52 (0.56)

^a $\Delta d_{001} = d_{001} - 0.96$ nm, which is basal spacing of organic-montmorillonite hybrid materials.

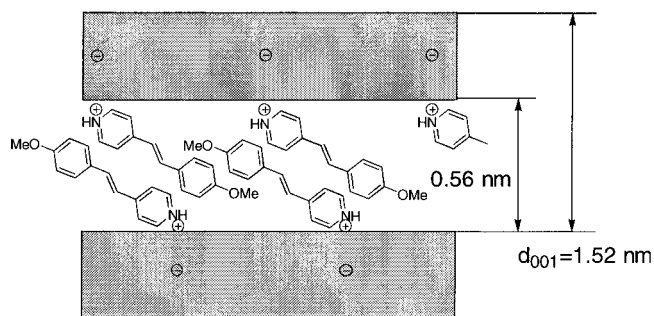


Figure 3. The orientation of the STZ molecules intercalated in montmorillonite in powder and in a silica matrix. The tilt angle of the STZ molecules to the clay layers plane were estimated at 23.4°.

LPy may exhibit conformational changes. Parts a and b of Figure 2 show simplified drawings of the orientation of the clay particles with the included guest molecules having a long alkyl chain, for the powder sample and the sol-gel composite film, respectively.

Figure 3 also shows the orientation of the STZ molecules in montmorillonite in which the d_{001} value does not change. It was calculated that the STZ molecular length is 1.41 nm along the molecular axis. In the STZ-montmorillonite hybrid materials, the layer distance was 0.56 nm, and the tilt angle of the STZ molecules was estimated to be 23.4° against the clay layer surface.

(d) Scanning Electron Microscopy (SEM) Observation of the Polysilicate Thin Films. Figure 4a,b

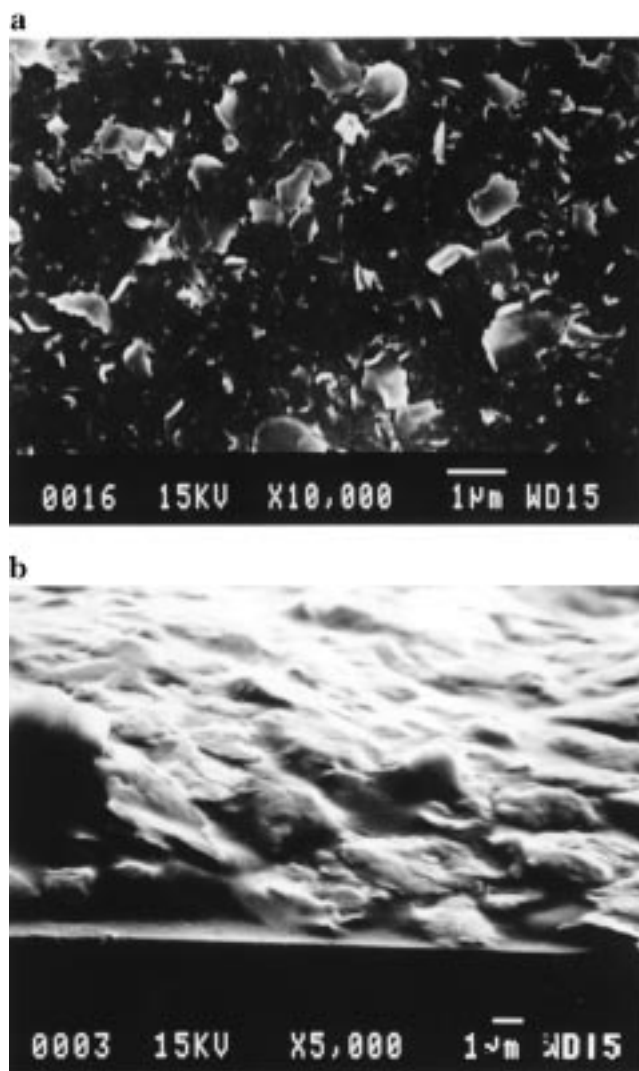


Figure 4. SEM photographs of the surface (a) and the cross section (b) of the polysilicate thin films involving dispersed STZ-montmorillonite hybrid particles. The organic-clay hybrid particles were dispersed as platelets of around 1 μ m width in the silica matrix and were aligned almost parallel to the substrate.

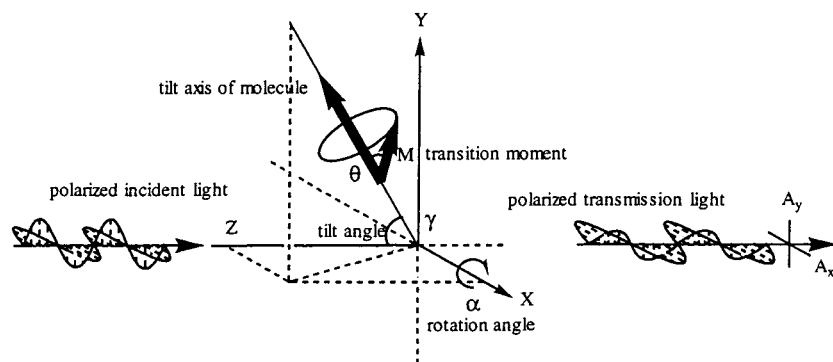


Figure 5. Schematic illustration of the polarized absorption instrument. The substrate is located parallel to the XY plane and rotates around the X axis.

shows SEM photographs of the surface and cross section of the silica glass films dispersed with STZ–montmorillonite hybrid particles. It can be seen that the organic–clay hybrid particles are dispersed as platelets of around $1\ \mu\text{m}$ width in the silica matrix and are aligned almost parallel to the substrate. It is well-known that Na–montmorillonite can be easily dispersed and swollen in aqueous solution, and a multilayered structure can be obtained by the casting of the suspension.¹⁶ The organic–clay hybrid materials can also be dispersed and swollen in polar organic solvents. In this experiment, dimethylformamide (DMF) was used as the solvent to act as the drying control chemical additive (DCCA) for the silica gel film which prevents cracking by lowering the surface tension.¹⁷ By spin coating the suspension in DMF, the clay particles formed a lamella which was oriented parallel to the substrate under centrifugal forces. It was, therefore, expected that anisotropic optical behavior for the polarized light can be attained in the bulk form of the thin film.

(e) Polarized Absorption Spectra of the Polysilicate Thin Films. The aggregation and self-assembly of the intercalated guest molecules was observed within the clay layers, and by measurement of the polarized absorption spectra of the guest molecules in the region of UV–vis and IR, the orientation of the intercalated guest molecules in the thin films could be clearly determined.^{18–20} UV absorbance was proportional to the square of the optical transition moment²¹ of the organic molecules, when the light quanta is incident along with the moment. Here, the optical transition moment is closely related with the average value of molecular dipole moments during an electronic transition caused by an interaction with the electric field of incident UV light. When the organic molecules are systematically orientated in the films, the absorption intensity changes, in accordance with a change in the angle between the incident light and the optical transition moment. Thus, the angle dependency of the absorption intensity can be evaluated by using polarized incident light. Figure 5 shows a schematic illustration

of the polarized absorption instrumentation diagram.²² The absorbance ratios of the two perpendicular polarized incident lights are represented by $R_{yx} = A_y/A_x$, where A_y and A_x represent the absorption intensities for the vertical and horizontal polarized incident lights, respectively. The R_{yx} values are given as

$$R_{yx} = \{2[\sin^2 \vartheta + \sin^2 \alpha(3 \cos^2 \vartheta - 1)] - (3 \sin^2 \alpha - 1)(3 \cos^2 \vartheta - 1) \sin^2 \gamma\} / \{2 \sin^2 \vartheta + (2 - 3 \sin^2 \vartheta) \sin^2 \gamma\} \quad (1)$$

where θ , α , and γ represent the angle of the molecular axis to the optical transition moment, the rotation angle of the substrate for the X axis, and the tilt angle of the molecule to the substrate normal, respectively. The film has an optical anisotropy due to the orientation of the guest molecules, as the R_{yx} values varied according to angle α . The tilt angle of the molecules (γ), representing the tilt angle from the normal line of the glass slide surface, was estimated using eq 1, while θ was determined from the MO calculations of PM3 and ZINDO.^{23–27} For example, the angle (θ) of the molecule axis to the transition moment measured at 380 nm of the STZ cation molecules was determined to be 9.2° .

Figure 6 shows the experimental correlation between R_{yx} and α of the polysilicate films dispersed with STZ–montmorillonite and the clay film of STZ–montmorillonite measured at a maximum absorbance wavelength of 380 nm. For the clay film shown in Figure 6, the R_{yx} values were almost constant, even when α was changed, implying that the clay film has no optical anisotropic character. The clay particles in the film are not aligned, causing the guest STZ molecules to exist in random orientation.

In contrast to the case of the clay film, the R_{yx} values of the polysilicate thin films prepared by spin-coat procedures have a maximum which gradually decreases as the α values increase or decrease. These results indicate that the STZ molecules are orientated not only in the clay layers but also subsequently on the silica glass slide, since the hybrid clay particles are aligned in the film coating. By fitting eq 1 to the correlation between R_{yx} and α , the tilt angle (γ) was estimated to

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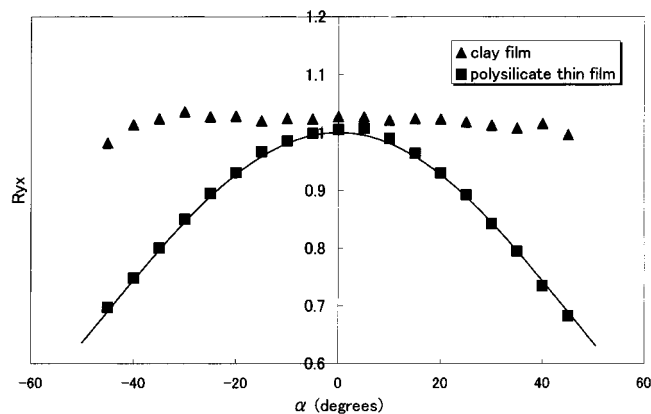


Figure 6. The experimental relationship between R_{yx} and α of the polysilicate thin films involving dispersed STZ–montmorillonite hybrid particles and the clay film of the particles from the DMF solvent at the point of the maximum absorbance wavelength of the STZ molecules, and the solid line of the calculated curve from eq 1 when γ and θ are 67° and 9.2° , respectively.

be 67° (Figure 6, solid line). In summary, the tilt angle of the STZ molecules to the glass slide was determined to be 23° , which is in good agreement with the X-ray results, and it was concluded that the plates of the hybrid materials are aligned almost parallel to the substrate. The films obtained in this study were confirmed to exist in anisotropic character in the orientation of STZ as analyzed by the results of SEM observations and the polarized absorption spectra. Figure 7 is a simplified representation of the polysilicate thin films with dispersed STZ–montmorillonite hybrid particles.

Conclusions

In this study, montmorillonite clay powders packed with several kinds of organic molecules were dispersed in the polysilicate network and spread on glass slides as a transparent film. It has been demonstrated that

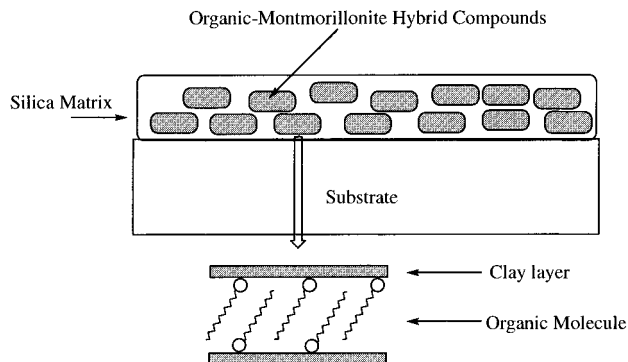


Figure 7. A simplified drawing of the polysilicate thin films involving dispersed organic–clay hybrid particles. The plates of the hybrid materials are aligned almost parallel to the substrate, and the organic guest molecules are totally oriented on the substrate.

the film can exhibit a desirable orientation by adopting a spin-coating procedure. The anisotropic orientation of the organic molecules were confirmed by polarized absorption spectroscopy, showing that excellent orientations of the organic molecule, clay, and substrate can be successfully achieved by dispersion in three-dimensional silica matrixes. The present methodology shows much promise for applications of clay minerals in the development of optical devices.

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