



Pergamon

Tetrahedron 56 (2000) 6979–6984

TETRAHEDRON

Photochromism in Oriented Thin Films Prepared by the Hybridization of Diarylethenes in Clay Interlayers

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Received 5 February 2000; revised 28 March 2000; accepted 30 March 2000

Abstract—The photochromism of 1,2-bis(2-methyl-3-thiophenyl)perfluorocyclopentene bearing two pyridinium substituents at each thiophenyl ring (**1**) in smectite clay thin films is the subject of the present study. In order to prepare oriented thin films with photochromic characteristics, the hybridization of cationic diarylethene molecules, **1**, into the layered clay was carried out, and the structure and photochromic properties of these hybrid materials were investigated. Clay intercalated diarylethene exhibited typical photochromic behavior. Polarized spectroscopic data has confirmed the diarylethenes inside the clay to be present as a tilted monolayer. Although the photochromic efficiency of these hybrid materials gradually decreased upon repeated irradiation with alternative UV and visible light, photochromic degradation could be dramatically improved by the cointercalation of cationic surfactant molecules such as dodecylpyridinium ions. © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

The development of photon-mode memory devices by utilizing organic photochromic compounds will lead to devices with fast response, high sensitivity, and large capacity. Since almost all organic photochromic compounds have thermal reversibility and poor durability after constant alternative UV–Vis light irradiation, these compounds are as yet unfavorable for such practical photon-mode memory devices.^{1–15} Recently, Irie et al.¹³ have been successful in the synthesis of diarylethene derivatives, which are thermally stable yet photochemically interconvertible with their closed-ring isomers. They have so far been shown to be one of the most promising materials in realizing the development of photo-mode memory devices having photochromic characteristics. It is important, however, that such materials are able to show facile photochromism in solid and solid-like systems for applications in such advanced memory devices. Moreover, in the development of thermally stable photochromic materials, efficient photochemical interconversions are essential in the integrated solid state.

Clay materials, i.e. negatively charged multilayered materials, possess a two-dimensional space, and various intercalated ionic or polar organic molecules can be accommodated within these interlayer spaces by ion-exchange reactions.^{16–18} Intercalated guest molecules have thus far

been found to intercalate as self-assembled aggregates.^{16–20} These unique and useful properties should open the way towards applications in many promising functional devices in the field of materials science.^{21–34}

The present investigation reports on the intercalation of cationic diarylethene derivatives into clay interlayers, and the resulting photochromic properties observed in solid and solid-like systems. In order to clarify the orientation structure of the intercalated diarylethene in clay thin films, UV/visible polarized spectroscopy was applied to the present clay–diarylethene hybrid materials. In addition, the durability of the photochromic reversibility against the alternative and repeated UV–Vis irradiation as well as the coadsorption effect of the surfactants added to this system to improve the photochromic reversibility have been discussed.

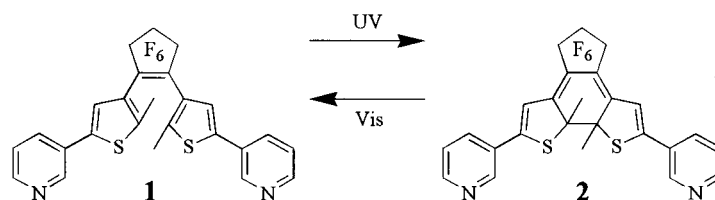
Experimental

Synthesis of cationic diarylethene^{35–37}

A cationic diarylethene, 1,2-bis(2-methyl-5-pyridylthiophene-3-yl)perfluorocyclopentene (**1**), was synthesized by the reaction of 2-(3-pyridinyl)-4-lithio-5-methylthiophene with perfluorocyclopentene at -78°C in accordance with a modified method reported by Cilat et al.^{36,37} The reaction mixture was extracted with chloroform, followed by condensation in vacuo resulting in a blue viscous liquid with a yield of 33%. The liquid was purified by column chromatography on silica gel (hexane/ethylacetate=1:3):

Keywords: photochromism; diarylethenes; clay hybrids; oriented thin films.

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Scheme 1.

^1H NMR (200 MHz, TMS) δ 2.01 (s, 2H), 2.53 (s, 1H), 7.33 (s, 1H), 7.28 (m, 1H), 7.80 (m, 1H), 8.54 (m, 1H), 8.81 (m, 1H). Compound **1** is well known to have two conformers, i.e. the *photoactive anti-parallel* and *photoinactive parallel* forms.³⁸ The doublet signals at 2.09 and 2.36 ppm are assigned to methyl protons at the 2 and 4 positions of the thiophene rings in the *anti-parallel* and *parallel* conformations, respectively.³⁸ NMR measurements indicate that the present compound **1** has two conformations in almost 1:1 ratio.

Synthesis of clay–diarylethene hybrid materials

Clay–diarylethene hybrid materials were synthesized by ion exchange with an organic cationic species in solution. Montmorillonite clay (Kunipia F) [$\text{Na}_{0.33}(\text{Al}_{1.67}\text{Mg}_{0.33})\text{SiO}_4(\text{OH})_2 \cdot n\text{H}_2\text{O}$] with a cation exchange capacity (CEC) of 1.19 mequiv./g was supplied by Kunimine Ind., Ltd and used without further purification. Laurylpyridinium chloride (Lpy) was used as the cationic surfactant. 0.2 mL of hydro-

chloric acid (1 equiv./L) was added to 10 mL of a methanol solution containing 0.1 mmol of the compound **1**, and stirred for the protonation of the two-pyridine groups. This solution was then diluted ten times with distilled water, producing the **1** stock solution (1 mmol/L **1** in 10% methanol solution). A stock suspension of montmorillonite in distilled water (84 mg/100 mL) was prepared by sonication. Clay–**1** hybrid materials were synthesized by mixing the clay stock suspension with an appropriate amount of **1** stock solution, where the mole ratios between the cationic groups including the added **1** and the cation exchange site of the clay, $[\mathbf{1}]/[\text{Clay}]$, were adjusted at 0.01, 0.05, 1.0, 2.0 and 3.0. Clay–**1**–Lpy hybrid materials were similarly obtained by mixing clay, **1** and Lpy ($[\mathbf{1}]/[\text{Lpy}]/[\text{clay}]=0.2:0.8:1.0$) in water. After stirring overnight, these mixture suspensions were passed through a membrane filter with a pore size of 0.45 μm (Toyo Roshi Co.) to separate the clay powder from the organic species, washed several times with water, and then dried to powder in vacuo at room temperature.

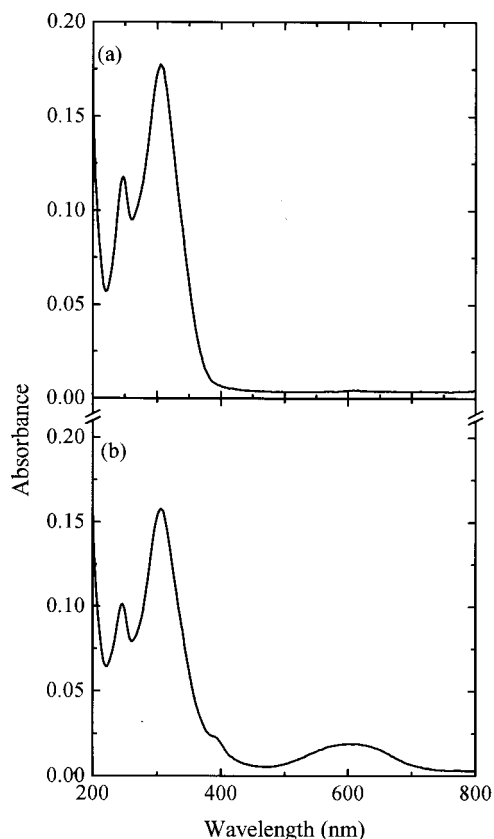


Figure 1. UV and visible absorption spectra of the open ring **1** (a) and closed ring **2** (b) molecules in 10% methanol aqueous solution.

Measurements

X-Ray diffraction analysis of the prepared powder samples was carried out with a RINT 2000 diffractometer (Rigaku) using $\text{CuK}\alpha$ radiation. The absorption spectra were recorded on a JASCO V-550 spectrophotometer. Spectroscopy with polarized light was performed by a JASCO V-550 spectrophotometer combined with a polarized unit attachment (JASCO RSH-452). Photochromic reactions were performed by irradiating the UV (300 ± 3 nm) and/or visible (600 ± 3 nm) light from a 150 W Xe lamp onto the monochromator.

Estimation of the quantum yields

The quantum yields were estimated by means of the potassium ferrioxalate actinometry.³⁹ A 150 W xenon lamp equipped with a monochromator (JASCO, Model FP-750 spectrofluorometer) was employed as a light source, which emits 300 ± 10 nm. In case of thin film as a sample, 2 mL of 100% **1** containing clay suspension was cast on a 20×40 mm² silica glass slide and dried by evaporation of the solvent. The resulting approximate circle thin film was irradiated by the above light source, inducing the decrease of the absorbance of the thin film monitored at around 645 nm. At the distance of 10 cm from the light source, the sample was placed and photolyzed to monitor the absorbance. The obtained quantum yields were the minimum of the value, as the reflection and scattering of light was neglected.

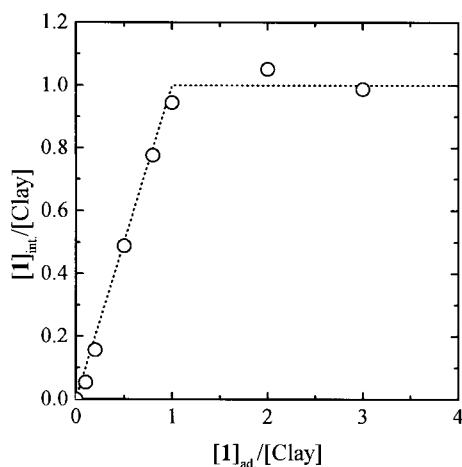


Figure 2. Isothermal adsorption curve of the **1** molecule in the clay interlayers.

Results and Discussion

Photochromism of **1** in 10% methanolic H₂O

Irradiation of **1** with light of 300 ± 3 nm resulted in the formation of a closed-ring form, **2**, which, upon irradiation

$$R = A_y/A_x = \frac{2[\sin^2 \theta + \sin^2 \alpha(3 \cos^2 \theta - 1)] - (3 \sin^2 \alpha - 1)(3 \cos^2 \theta - 1)\sin^2 \gamma}{2 \sin^2 \theta + (2 - 3 \sin^2 \theta)\sin^2 \gamma} \quad (1)$$

at 600 ± 3 nm, reverted to the starting **1** (Scheme 1).

The absorption spectra of the open ring **1** and closed **2** are shown in Fig. 1(a) and (b), respectively. Open ring **1** has two absorption maxima (ca. 250 and 300 nm) in the wavelength range of 200–600 nm. Upon irradiation of the colorless solution of open ring **1** with UV light (300 ± 3 nm), the solution rapidly turned to blue with an absorption maximum at around 600 nm accompanied by a shoulder at around 400 nm. The quantum yields for the ring closure of **1** to **2** was estimated as 0.3 at room temperature (See Experimental in detail). No change in color could be observed under dark conditions even when the blue colored solution was left standing at room temperature for a week. However, upon irradiation with visible light (600 ± 3 nm), the color disappeared and returned to the original **1**.

Intercalation of **1** to clay interlayers

Fig. 2 shows the plots of the amount of intercalated **1**, i.e. $[1]_{\text{int.}}$, against the amount of the added **1**, $[1]_{\text{ad.}}$, on the basis of the clay concentration, i.e. $[\text{Clay}]$. The diarylethene was

Table 1. Basal spacings d_{001} obtained from X-ray diffraction analysis

$[1]/[\text{Clay}]$ (mol%)	d_{001} (nm)
0	1.22
1	1.26
5	1.41
10	1.52
50	1.59
100	1.73

quantitatively intercalated within the clay interlayers at $[1]_{\text{ad.}}/[\text{Clay}] \leq 1$, i.e. until $[1]_{\text{ad.}}$ reached $[\text{Clay}]$. With the addition of $[1]$ exceeding $[\text{Clay}]$ (i.e. > 1.0), however, the amount of the intercalated **1** remained almost constant. This indicates that the intercalation of compound **1** in the clay interlayers may be due to the electrostatic interaction of the two pyridinium ions of **1** with the ion-exchange sites on the clay layer surfaces.

The basal spacings d_{001} estimated from X-ray diffraction analysis of the clay powders in the absence and presence of intercalated **1** are summarized in Table 1. The values of d_{001} , which are the basal spacings of the clay layers, increased from 1.22 to 1.73 nm with an increase in the $[1]_{\text{ad.}}/[\text{Clay}]$ ratios from 0 to 1.0, indicating that the clay interlayer space begins to open by the introduction of **1**, and that the packing conformation of the intercalated **1** are subject to change with the increase in the $[1]/[\text{Clay}]$ ratios.

Assuming that guest molecules with chromophores are regularly aligned in the thin film of clay minerals, angle γ between the normal line of the glass plate and the long molecular axis could be evaluated by spectroscopy with polarized light.^{40,41} Angle γ can be expressed by the following equation:

where R is the dichroic ratio A_y to A_x in which they represent the absorption intensities for the horizontal and vertical polarized incident lights, respectively. θ and α represent the angles of the molecular axis to the optical transition moment, the angle between the incident light and the substrate plane. The film has an optical anisotropy due to the organized alignment of the molecules, as the R values varied according to angle α . Angle γ , therefore, was estimated using Eq. (1). Angle θ of the molecular axis to the optical transition moment, measured at 300 nm of **1**, was determined to be 28° , where the transition moments were deduced from MO calculations using PM3 and ZINDO/S.

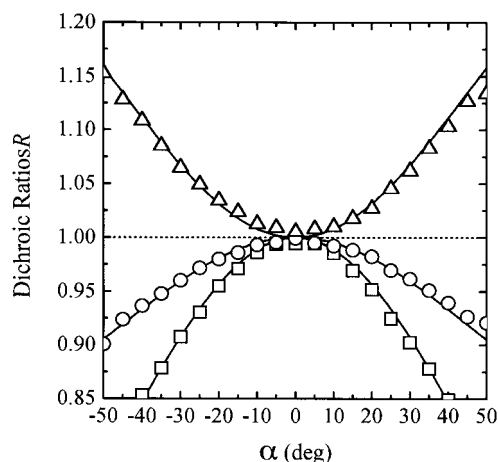


Figure 3. Dependence of incident angle α on the dichroic ratios R of the Clay–**1** hybrid thin films. $[1]/[\text{Clay}] = 1$ (\square), 5 (\circ), and 10 (\triangle) (mol%).

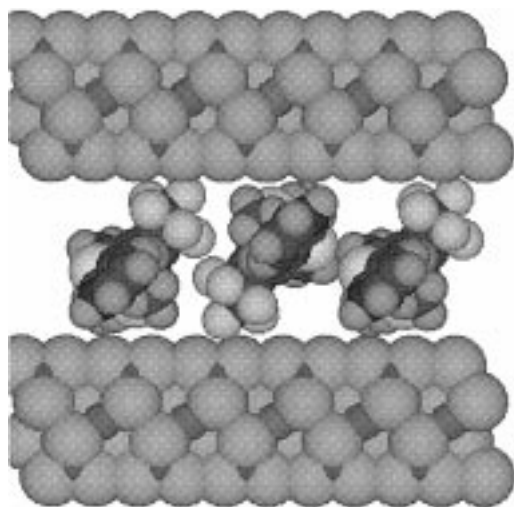
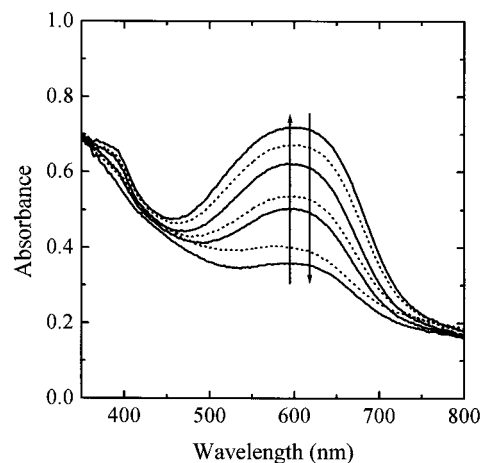
Table 2. Structural parameters obtained from polarized spectroscopy

[1]/[Clay] (mol%)	γ ($^\circ$)	Θ_T ($^\circ$)	d_{001}^{PS} (nm)	d_{001}^{XRD} (nm)
1	60.5	23.9	1.39	1.26
5	57.0	30.0	1.50	1.41
10	51.5	40.9	1.67	1.52
100	–	(45.5)	–	1.73

Fig. 3 shows the experimental correlation between R and α of the Clay–**1** (a) hybrid thin films prepared by casting the aqueous suspension of the Clay–**1** hybrid materials ($[1]_{ad}/[Clay]=0.01, 0.05$ and 0.10) on the glass plates. The R values of all the hybrid samples depended on the α values, and had a maximum or minimum at $\alpha=0^\circ$. This shows that **1** is oriented not only in the clay interlayers but also on the glass plates, i.e. the Clay–**1** hybrid materials are aligned within the thin films. Angle γ estimated by fitting Eq. (1) to the correlation between R and α is summarized in Table 2. The obtained tilt angle (Θ_T) of **1** to the glass plate was in good agreement with the X-ray results under the assumption that the cation of **1** electrostatically interacts with the intraplanar-exchangeable sites, and it was concluded that the plates of the hybrid materials are aligned almost parallel to the substrate. These results indicate that the intercalated **1** molecules are inclined at Θ_T in the clay interlayers at a given $[1]_{ad}/[Clay]$ ratio. These results indicate that angle Θ_T is 45.5° at $[1]/[Clay]=1.0$. A plausible structural model of **1** in the clay interlayers at $[1]/[Clay]=1.0$ is shown in Fig. 4. This structural analysis suggests that **1** forms an inclined interdigit aggregate in the clay layer spaces.

Photochromism of **1** in the clay interlayers

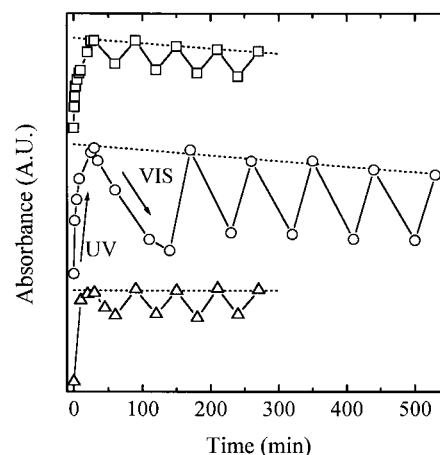
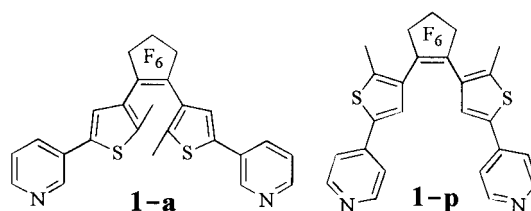
The synthesized Clay–**1** hybrid thin film exhibited absorption spectra, as shown in Fig. 5, when irradiated with UV (solid line) or visible (broken line) light. An increase and decrease in the absorbance at 600 nm could be observed by UV and visible light irradiation, a characteristic behavior of photochromism, which is similar to the case in solution. The quantum efficiencies of the coloration in this thin film with 100% loading of **1** were estimated to not less than 0.12 at room temperature. The incident light quanta were not

**Figure 4.** A plausible structural model of the open ring **1** molecules in the clay interlayers at $[1]/[Clay]=1.0$.**Figure 5.** Absorption spectra of Clay–**1** hybrid powders during UV (solid) or visible (broken) irradiation at $[1]/[Clay]=1.0$.

corrected by subtracting a fraction of light scattering, reflection, and absorption on the surface of the clay thin films.

During alternative irradiation of the Clay–**1** hybrid thin films by UV and visible light, the retrieval percentages of the closed ring **2** as well as the open ring **1** decreased, as can be seen in Fig. 6. It has been reported by Irie et al. that the present diarylethene-type molecules exist as *parallel* (**1-p**) and *anti-parallel* (**1-a**) isomers (Scheme 2).³⁸

Among them only **1-a** was photochemically interconvertible with **2**, while **1-p** is assumed to be inert against UV

**Figure 6.** Irradiation time dependence of the absorbance at 600 nm with repeated UV or visible light irradiation. $[1]/[Clay]=0.2$ (\square) and 1.0 (\circ), and $[1]:[Lpy]:[Clay]=0.2:0.8:1.0$ (\triangle).**Scheme 2.**

irradiation.³⁸ **1** was shown to be an almost equal mixture of **1-p** and **1-a**, which was identified by NMR spectroscopy, as described in Experimental. Intercalated open ring **1-a** was subsequently photochemically closed to be **2** by UV irradiation. Once the ring opening of **2** took place upon visible light irradiation, a reversion mainly to the starting **1-a** can be seen accompanied to some extent by the formation of a photochemically inert isomer. That is, less than 10% of the opening of the ring of **2** led to **1-p** during several repeated interconversions. This is explicable by the intercalation behavior of **1** on the clay layer surfaces. That is, both of the two pyridinium cations of **1** are adsorbed on the same clay surface with an electrostatic interaction having a distance of ca. 1.3 nm, which is almost comparable to that of the average adjacent anionic sites on the clay surfaces (0.9 nm). In contrast, a rather better agreement can be seen in the case of the *parallel* form which has two pyridinium groups located at ca. 1.0 nm interacting with the anionic sites of the clay surface. It may now be concluded that the lowering of the reversibility of the photochromism can be attributed to this entrapment of **1** as a photochemically inert **1-p** in the clay interlayers.

In order to suppress the formation of photoinactive parallel open ring **1-p**, it can be expected that the vacant anionic sites are buried by the other intercalants. Lpy cations were cointercalated into the clay interlayers with **1** to remove the vacant sites of the clay surfaces. Fig. 6 shows an improvement in the reversibility between **1** and **2** by the coadsorption of Lpy with **1**. Compared with the Clay-**1** hybrid materials in the absence of Lpy, the amounts of the closed ring **2** did not change even after recycling operations were carried out by irradiation with alternative UV and visible light. These results indicate that the coadsorption of Lpy molecules is remarkably effective in achieving the photochromic reversibility of Clay-**1** hybrid materials. At [1]/[Lpy]=0.4, intercalated **1** is completely surrounded by Lpy molecules and, therefore, without any intermolecular interaction of the **1** molecules. Since the intercalated Lpy molecules are well known to form closely packed interdigit aggregates in the clay interlayers,¹⁸ intercalated **1** shows special restrictions in movement by the cointercalation of Lpy. Thus, the formation of the photoinactive parallel open ring **1** is suppressed, since **1** may occupy a large space within the clay interlayers, being bulkier molecules compared with the anti-parallel form, **1-a**. These results clearly indicate that the cointercalation of Lpy molecules improved the photochromic characteristics of the Clay-**1** hybrid materials.

Conclusions

From X-ray diffraction and polarized spectroscopic analyses, it was observed that intercalated **1** formed an interdigit aggregate structure with a tilt angle of ca. 45° against the clay surface with a coverage of 100%. The present Clay-**1** hybrid materials were found to exhibit efficient and smooth photochromism. The photochromism efficiency, however, decreased by repeated irradiation with alternative UV and visible light. This was attributed to the formation of the photoinactive parallel open ring **1**. However, this degradation could be suppressed and reversibility greatly

enhanced by cointercalating Lpy molecules into the clay interlayers with **1**.

Acknowledgements

The authors would like to thank Prof. Masahiro Irie of the Department of Applied Chemistry of Kyushu University for his generous supply of chemicals as well as his valuable advice. We would also like to acknowledge the Grant-in-aid for Scientific Research (B) of the Ministry of Education, Science, Sports and Culture of Japan.

References

1. The Chemical Society of Japan Chemistry of Organic Photochromism, Kikan Kagaku Sosetsu No. 28 Japan Scientific Societies: Tokyo, 1994.
2. Takagi, K.; Kurematsu, T.; Sawaki, Y. *J. Chem. Soc. Perkin Trans. 2* **1991**, 1517.
3. Ogawa, M.; Fujii, K.; Kuroda, K.; Kato, C. *Mater. Res. Soc. Symp. Proc.* **1991**, 233, 89.
4. Ogawa, M.; Ishikawa, A. *J. Mater. Chem.* **1998**, 8, 463.
5. Seki, T.; Ichimura, K. *Macromolecules* **1990**, 23, 31.
6. Irie, M.; Eriguchi, T.; Uchida, K. *Tetrahedron* **1997**, 53, 12263.
7. Bens, J. E.; Drysch, C. A. T. *J. Lumin.* **1998**, 76, 90.
8. Tsujioka, T.; Kume, T.; Irie, M. *J. Photochem. Photobiol. A* **1997**, 104, 3203.
9. Nakashima, N.; Nakanishi, T.; Irie, M. *Chem. Lett.* **1997**, 591.
10. Yamaguchi, T.; Uchida, K.; Irie, M. *J. Am. Chem. Soc.* **1997**, 119, 292.
11. Takeshita, M.; Irie, M. *Chem. Lett.* **1998**, 292.
12. Stellacci, F.; Bertarelli, C.; Zerbi, G. *Adv. Mater.* **1997**, 11, 292.
13. Kobatake, S.; Yamada, T.; Irie, M. *J. Am. Chem. Soc.* **1991**, 113, 2380.
14. Abe, S.; Yamazaki, I.; Irie, M. *Langmuir* **1997**, 13, 5504.
15. Takeshita, M.; Kato, N.; Irie, M. *J. Org. Chem.* **1998**, 63, 9306.
16. Grim, R. E. *Clay Mineralogy*, McGraw-Hill: New York, 1953.
17. Whittingham, M. S.; Jacobson, A. J. *Intercalation Chemistry*, Academic: New York, 1982.
18. The Chemical Society of Japan Microporous Crystals, Kikan Kagaku Sosetsu No. 21 Japan Scientific Societies: Tokyo, 1994.
19. The Chemical Society of Japan Fundamental and Advances in Photochemistry, Kikan Kagaku Sosetsu No. 36 Japan Scientific Societies: Tokyo, 1998.
20. Kanoh, T.; Shichi, T.; Takagi, K. *Chem. Lett.* **1999**, 117.
21. Ogawa, M.; Takahashi, M.; Kato, C.; Kuroda, K. *J. Mater. Chem.* **1994**, 4, 519.
22. Ogawa, M.; Handa, T.; Kuroda, K.; Kato, C.; Tani, T. *J. Phys. Chem.* **1992**, 96, 8116.
23. Sakoda, K.; Kiminami, K. *Chem. Phys. Lett.* **1993**, 216, 270.
24. Cooper, S.; Dutta, P. K. *J. Phys. Chem.* **1990**, 94, 114.
25. Ogawa, M.; Takahashi, M.; Kuroda, K. *Chem. Mater.* **1994**, 6, 715.
26. Ruiz-Hitzky, E. *Adv. Mater.* **1993**, 5, 334.
27. Govea, L. V.; Steinfink, H. *Chem. Mater.* **1997**, 9, 849.
28. Fujita, W.; Awaga, K. *J. Am. Chem. Soc.* **1997**, 119, 4563.
29. (a) Takagi, K.; Usami, H.; Fukaya, H.; Sawaki, Y. *J. Chem. Soc. Chem. Commun.* **1989**, 1174. (b) Usami, H.; Takagi, K.; Sawaki, Y. *J. Chem. Soc. Perkin Trans. 2* **1990**, 1732.

30. Usami, H.; Takagi, K.; Sawaki, Y. *J. Chem. Soc. Faraday Trans.* **1992**, *88*, 77.
31. Takagi, K.; Shichi, T.; Usami, H.; Sawaki, Y. *J. Am. Chem. Soc.* **1993**, *115*, 4339.
32. Shichi, T.; Takagi, K.; Sawaki, Y. *Chem. Commun.* **1996**, 2027.
33. Shichi, T.; Takagi, K.; Sawaki, Y. *Chem. Lett.* **1996**, 781.
34. Sasai, R.; Shin'ya, N.; Shichi, T.; Takagi, K.; Gekko, K. *Langmuir* **1999**, *15*, 413.
35. Gronowits, S.; Lwitz, K. *Chem. Scripta* **1984**, *24*, 5.
36. Gliat, S. L.; Kawai, S. H.; Lehn, J. M. *J. Chem. Soc., Chem. Commun.* **1993**, 1439.
37. Gilat, S. L.; Kawai, S. H.; Lehn, J. M. *Chem Eur. J.* **1995**, *1*, 275.
38. Irie, M.; Sakemura, K.; Okinaka, M.; Uchida, K. *J. Org. Chem.* **1995**, *60*, 8305.
39. Hatchard, C. H.; Parker, C. A. *Proc. R. Soc. (A)* **1956**, 234, 518.
40. Fukuda, K.; Kato, T.; Nakahara, H.; Shibasaki, Y. *Chohakunakubunshi Soshikimukunokagaku*, Kodansya: Tokyo, 1993.
41. Sonobe, K.; Kikuta, K.; Takagi, K. *Chem. Mater.* **1999**, *11*, 1089.