n acentric arrangement of *p*-nitroaniline molecules between the layers of olinite†

uyuki Kuroda,*[ab] Kouichi Hiraguri,[a] Yoshihiko Komori,[ab] Yoshiyuki Sugahara,[a] Haruyuki Mouri[c] and
hiaki Uesu[c]

epartment of Applied Chemistry, Waseda University, Ohkubo-3, Shinjuku-ku, Tokyo 169-8555, Japan.
-mail: kuroda@mn.waseda.ac.jp
agami Memorial Laboratory for Materials Science and Technology, Waseda University, Nishiwaseda-2,
hinjuku-ku, Tokyo, 165-0051, Japan
epartment of Physics, Waseda University, Ohkubo-3, Shinjuku-ku, Tokyo, 169-8555, Japan

eceived (in Cambridge, UK) 30th July 1999, Accepted 4th October 1999

Nitroaniline molecules were intercalated between the yers of kaolinite, and an acentric arrangement of *p*-itroaniline induced by the asymmteric environment of the nterlayer region was accomplished.

Layered materials have been utilized for immobilizing and organizing functional substances in their interlayer spaces to form supramolecular inorganic–organic hybrid systems.[1–3] The advantage of the use of layered materials is its confinement of guest species in their two-dimensional regions to induce selective orientation. A typical field demanding preferred orientation is nonlinear optics, using organic molecules with hyperpolarizabilities (β) like *p*-nitroaniline (*p*NA), which needs to be oriented noncentrosymmetrically.[4] To achieve an acentric arrangement of *p*NA, various hosts such as cyclodextrins,[5] and microporous and mesoporous molecular sieve hosts[6,7] have been utilized. Layered materials like layered double hydroxides,[8] saponite[9] and $MnPS_3$[10] have also been applied for the arrangement of molecules with hyperpolarizabilities such as *p*NA and stilbazolium ions. However, an outer electrical field[9] or guest-guest interactions[8,10] are needed for alignment of the molecules because the interlayer spaces of the layered materials are sandwiched between identical surfaces of adjacent layers.

Kaolinite has a unique layered structure because the interlayer region is sandwiched between the hydroxy groups of the $AlO_2(OH)_4$ sheets on one side and the oxide arrangements of the silicate sheets on the other[11] [Fig. 1(*a*)], affording an asymmetric nanoenvironment. Guest molecules like DMSO are easily intercalated and aligned in one direction between the layers of kaolinite.[12] Thus, kaolinite is an excellent host material for organizing supramolecular hybrid systems. Here we report the successful formation of a kaolinite–*p*NA intercalation compound and its nonlinear optical properties.

The kaolinite [ideal chemical formula, $Al_2Si_2O_5(OH)_4$] used was KGa1, a highly crystalline Georgia kaolinite obtained from the Source Clays Repository of the Clay Minerals Society (USA).[13] The reactivity of kaolinite for intercalation is very low due to the inherent hydrogen bonding between the layers. Although small polar molecules such as DMSO can be intercalated directly,[14] *p*NA has been reported not to be intercalated into kaolinite.[15] In order to overcome this obstacle, a fine guest displacement method using a kaolinite–methanol intercalation compound as the intermediate was applied (Fig. 1).[16–18] To synthesize a kaolinite-methanol intercalation compound, a kaolinite–*N*-methylformamide (NMF) intercalation compound was prepared and treated repeatedly with methanol eight times to displace NMF completely.[15] The wet kaolinite–methanol intercalation compound (1 g) was stirred in a CH_2Cl_2 solution of *p*NA (0.60 g *p*NA per 20.0 ml CH_2Cl_2) at room temperature for 3 days to form the kaolinite–*p*NA intercalation compound.

The intercalation of *p*NA molecules between the layers of kaolinite was proved by powder X-ray diffraction (Fig. 2). The basal spacing of kaolinite is 0.72 nm and it increased to 1.50 nm in the kaolinite–*p*NA intercalation compound, the value of which was larger than that of the kaolinite–methanol intercalation compound (1.11 nm). The increase of 0.78 nm after intercalation is smaller than the length of the *p*NA molecules (0.90 nm). Considering the amount of *p*NA (24 mass%), which corresponds to $pNA/Al_2Si_2O_5(OH)_4 = 0.6$, the *p*NA molecules are thought to take a monomolecular arrangement, with their molecular axis inclined to the aluminosilicate layers by *ca.* 60° [Fig. 1(*b*)].

In the ^{13}C CP/MAS NMR spectrum of the product, typically four signals due to the aromatic ring carbons of *p*NA were observed at δ 112, 128, 135 and 155,† indicating that the *p*NA molecules were incorporated into the kaolinite. On the other hand, a signal at δ 49 was observed which was assigned to CH_3O, suggesting that a small amount of methanol or methoxy groups attached to the octahedral sheets were present.

The main driving force for the intercalation of *p*NA into kaolinite is thought to be hydrogen bonding between the

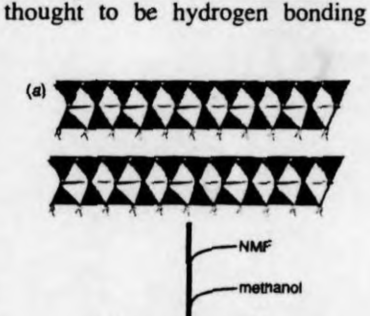

Fig. 1 (*a*) Structure of kaolinite (ref. 11) and (*b*) ideal structure of kaolinite–*p*NA intercalation compound.

---

† ^{13}C and ^{29}Si CP/MAS NMR and IR spectral data for the kaolinite–*p*NA intercalation compound are available from the RSC web site, see http://www.rsc.org/suppdata/cc/1999/2253/

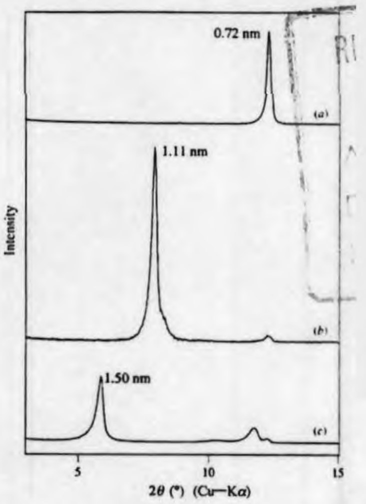

Fig. 2 X-Ray diffraction patterns of (*a*) kaolinite, (*b*) kaolinite–methanol intercalation compound and (*c*) kaolinite–*p*NA intercalation compound.

Table 1 SHG efficiency (referenced to urea) of the samples

Sample	SHG intensity
*p*NA	same level as background
Kaolinite	same level as background
Kaolinite–*p*NA intercalation compound	0.93
Mixture of kaolinite and *p*NA[a]	same level as background
Mixture of kaolinite and *p*NA[b]	0.03–0.05

[a] A physically ground mixture of kaolinite and *p*NA powders. [b] A mixture prepared by dispersing kaolinite with a THF solution of *p*NA.

electrophilic NO_2 groups of *p*NA and the hydroxy groups of kaolinite, which is supported by the intercalation behavior of nitrobenzene and aniline. It was found that nitrobenzene molecules were intercalated between the layers of kaolinite (the basal spacing increased to 1.46 nm) whereas aniline molecules were not.[19] However, the interactions between the NH_2 groups of *p*NA and the silicate sheets of kaolinite presumably contribute to the formation of the kaolinite–*p*NA intercalation compound, because no intercalation reaction took place with *N*,*N*-dimethyl-*p*-nitroaniline.[20]

The interactions between the silicate sheets and the *p*NA molecules were investigated by solid state ^{29}Si NMR spectroscopy.† The Q^3 environments of Si in the tetrahedral silicate sheets of kaolinite showed a signal at around $\delta -91$ with a slight splitting,[21] whereas that of the kaolinite-*p*NA intercalation compound showed the signal shifted to δ −91.5 without splitting. The chemical shift is the same as those observed for kaolinite–alkylamine intercalation compounds (for example, δ −91.5 for an octylamine–kaolinite intercalate) where NH_2 groups interact with the silicate sheets, suggesting that similar interactions are occurring with *p*NA. The IR spectrum of the kaolinite–*p*NA intercalation compound showed that the bands due to $\nu(NH_2)$ at 3494 and 3402 cm^{-1} are shifted to higher wavenumbers than those for *p*NA crystals (3482 and 3361 cm^{-1}).† These findings indicate the presence of weaker hydrogen bondings between NH_2 groups and silicate sheets as compared with those in *p*NA crystals.

The second harmonic generation (SHG) intensities of the materials treated here are shown in Table 1.[22] The kaolinite–*p*NA intercalation compound is SHG active and its intensity is similar to that of urea. No SHG signals were observed for *p*NA crystals, because their second order nonlinear susceptibility is cancelled by their centrosymmetric structure ($P2_1/n$).[23] Almost no signals were observed for kaolinite and a physical mixture of kaolinite with crystalline *p*NA powder where the *p*NA powder was adsorbed only on the outer surface of the kaolinite particles. When *p*NA was dissolved in THF and the solution was mixed with kaolinite to form a mixture where the *p*NA molecules were spread over the outer surface of the mineral, the SHG intensity of the mixture was less than 0.05. Consequently, the observ SHG intensity of the intercalation compound is almost entire ascribable to *p*NA molecules in the interlayer space of kaolin the interactions between the unique interlayer structure kaolinite and the *p*NA molecules induce the noncentrosymmetric orientation of *p*NA molecules exclusively. Althoug there are no definitive data on the degree of noncentrosymmetric orientation of the *p*NA molecules, the present resu show that kaolinite is an excellent host for immobilizi photofunctional materials in its unique interlayer region. T effect of *p*NA loading on the properties and the preparation thin films are now under investigation.

The spontaneous arrangement of guest molecules by interlayer surface structure is a further step towards high selective catalytic reactions, stereoselective organic synthes and the formation of specific molecular assemblies with unus chemical, photochemical and electrical properties, which w be increasingly important for nanomaterials design for vanced technological applications.

This work was financially supported by a Grant-in-Aid f Scientific Research from the Ministry of Education, Scienc Sports and Culture of the Japanese Government. The autho thank Mr Ryoji Takenawa for experimental assistance.

Notes and references

1 *Inorganic Materials*, 2nd edn., ed. D. W. Bruce and D. O'Hare, Wile New York, 1996.
2 M. Ogawa and K. Kuroda, *Chem. Rev.*, 1995, **95**, 399.
3 G. Alberti and T. Bein, *Comprehensive Supramolecular Chemis* Pergamon, Oxford, 1996, vol. 7.
4 P. N. Prasad and D. J. Williams, *Introduction to Nonlinear Optic Effects in Molecules and Polymers*, Wiley, New York, 1991.
5 S. Tomaru, S. Zembutsu, M. Kawachi and M. Kobayashi, *J. Chem. So Chem. Commun.*, 1984, 1207; D. F. Eaton, *Tetrahedron*, 1987, 4 1551.
6 S. D. Cox, T. E. Gier, G. D. Stucky and J. Bierlein, *J. Am. Chem. So* 1988, **110**, 2986; S. D. Cox, T. E. Gier and G. D. Stucky, *Chem. Mate* 1990, **2**, 609; L. Werner, J. Caro, G. Finger and J. Kornatowski, *Zeolit* 1992, **12**, 658.
7 I. Kinski, H. Gies and F. Marlow, *Zeolites*, 1997, **19**, 375.
8 S. Cooper and P. K. Dutta, *J. Phys. Chem.*, 1990, **94**, 114.
9 M. Ogawa, M. Takahashi and K. Kuroda, *Chem. Mater.*, 1994, 715.
10 P. G. Lacroix, R. Clément, K. Nakatani, J. Zyss and I. Ledoux, *Scien* 1994, **263**, 658; T. Coradin, R. Clément, P. G. Lacroix and K. Nakata *Chem. Mater.*, 1996, **8**, 2153.
11 E. Akiba, H. Hayakawa, S. Hayashi, R. Miyawaki, S. Tomura, Shibasaki, F. Izumi, H. Asano and T. Kamiyama, *Clays Clay Mine* 1997, **45**, 781.
12 J. G. Thompson and C. Cuff, *Clays Clay Miner.*, 1985, **33**, 490.
13 S. W. Bailey, *Crystal Structures of Clay Minerals and Their X-R Identification: Structure of Layer Silicates*, ed. G. W. Brindley and Brown, Mineralogical Society, London, 1980, pp. 1–39.
14 B. K. G. Theng, *The Chemistry of Clay-Organic Reactions*, Ad Hilger, London, 1974, pp. 1–260.
15 J. Tunney and C. Detellier, *Can. J. Chem.*, 1997, **75**, 1766.
16 Y. Komori, Y. Sugahara and K. Kuroda, *J. Mater. Res.*, 1998, 930.
17 Y. Komori, Y. Sugahara and K. Kuroda, *Chem. Mater.*, 1999, **11**, 3
18 Y. Komori, Y. Sugahara and K. Kuroda, *Appl. Clay Sci.*, 1999, 241.
19 Intercalation of nitrobenzene and aniline was performed by stirring kaolinite–methanol intercalation compounds in those liquids at ro temperature for 3 days.
20 Intercalation reaction was attempted by stirring a wet kaolinit methanol intercalation compound in a saturated CH_2Cl_2 solution of *N*, dimethyl-*p*-nitroaniline at room temperature for 3 days.
21 P. F. Barron, R. L. Frost, J. O. Skjemstad and A. J. Koppi, *Nature*, 19 **302**, 49.
22 The SHG properties were measured with incident light of λ = 1.064 from a Nd:YAG laser; the intensity of the transmitted second harmo wave of λ = 0.532 μm was detected. Samples were ground to p through a 100 mesh sieve and packed on a glass slide to the thickness 0.15 mm.
23 K. N. Trueblood, E. Goldish and J. Donohue, *Acta Crystallogr.*, 19 **14**, 1009.

Communication 9/0620