An acentric arrangement of *p*-nitroaniline molecules between the layers of kaolinite†

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p-**Nitroaniline molecules were intercalated between the layers of kaolinite, and an acentric arrangement of *p*-nitroaniline induced by the asymmteric environment of the interlayer 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$_2$Si$_2$O$_5$(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$_2$Cl$_2$ solution of *p*NA (0.60 g *p*NA per 20.0 ml CH$_2$Cl$_2$) 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 *p*NA/Al$_2$Si$_2$O$_5$(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
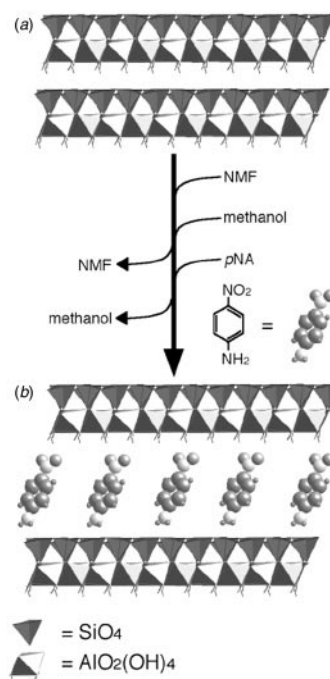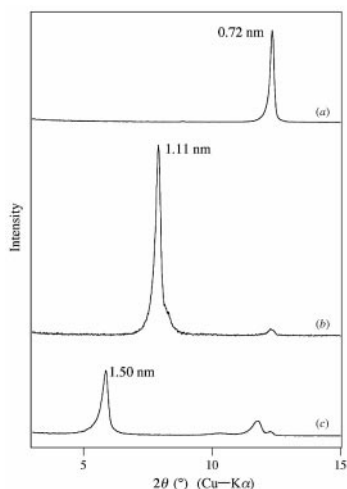

Fig. 1 (*a*) Structure of kaolinite (ref. 11) and (*b*) ideal structure of kaolinite–*p*NA intercalation compound.

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 $\delta -91.5$ without splitting. The chemical shift is the same as those observed for kaolinite–alkylamine intercalation compounds (for example, $\delta -91.5$ 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 observed SHG intensity of the intercalation compound is almost entirely ascribable to *p*NA molecules in the interlayer space of kaolinite; the interactions between the unique interlayer structure of kaolinite and the *p*NA molecules induce the noncentrosymmetric orientation of *p*NA molecules exclusively. Although there are no definitive data on the degree of noncentrosymmetric orientation of the *p*NA molecules, the present results show that kaolinite is an excellent host for immobilizing photofunctional materials in its unique interlayer region. The effect of *p*NA loading on the properties and the preparation of thin films are now under investigation.

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

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