# Synthesis of Novel Nano-structured Clays: Unique Conformation of Pillar Complexes

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Novel nano-structured clays were synthesized from cation exchange reaction by the intercalation of rhodium complexes with ligand spacers into clay. Expansion of interlayer space of the modified clays depends on the spacers. A unique conformation of pillar complexes was detected by cross polarization magic angle spinning (CP MAS) NMR.

Inorganic–organic hybrids have been gaining much attention from the viewpoint of functional materials.[1,2] Host–guest interactions between inorganic layer compounds and organic compounds give a great potential to construct novel nano-structural materials. Among the inorganic layer compounds, the clay minerals have prosperous properties such as facile intercalation of polar guest molecules and cations, reversible lamination and delamination, and swellability.[3,4] Moreover, the enhancement of molecular recognition reactions such as shape selective, regioselective, and asymmetric reaction can be expected because of the limited interlayer space and the immobilization of the stereochemistry of the active species and guest substrates by using smectite clays as a host.[5,6] The nano-sized reaction space can be also constructed in smectites. The nano-sized reaction space plays an important role in the selective catalytic reactions. In the previous papers, we described asymmetric hydrogenation by smectite-intercalated chiral rhodium complexes and multiple modified smectites.[6–9]

In this paper, we report the synthesis of novel nano-structured clays by the intercalation of rhodium complex with long alkyl chains (pillar complex) into smectites. We found all-*trans* conformation for the alkyl groups of the pillar complexes in the smectite layer by solid-state NMR measurements and the remarkable enhancement of their crystallinity.

4,4′-dialkyl-2,2′-bipyridine (*Cn*-bpy, $n = 1$–23) ligand was synthesized from 4,4′-dimethyl-2,2′-bipyridine (*C1*-bpy) and adequate alkyl bromide as in the literature.[10] Pillar complex [Rh(COD)*Cn*-bpy]$ClO_4$ (COD = 1,5-cyclooctadiene) was synthesized from *Cn*-bpy, $[Rh(\mu\text{-}Cl)(COD)]_2$ and $AgClO_4$ (Rh-*Cn*-bpy). Pillar complex (1.0 equiv. of cation exchange capacity) was intercalated into taeniolite (Rh-*Cn*-bpy/TN) by cation exchange as follows: Pillar complex in acetone (120 mL) was added into lithium taeniolite (LiTN,[11] cation exchange capacity = 268.2 mequiv. $(100\,g)^{-1}$, Topy Industries) swollen with deionized water (30 mL), followed by stirring for 48 h at ambient temperature.

X-ray diffraction (XRD) measurements revealed that the basal spacing of the nano-structured clay was expanded after the intercalation (Figure 1). Generally, clays intercalated with large metal complexes show low crystallinity.[12] Except for Rh-*C1*-bpy/TN (Figure 1A (b)), modified taeniolite with long alkyl chains ($n > 7$) showed sharp diffraction peak comparable to the original taeniolite (Figure 1A (a)). The high crystallinity of clay layers could be achieved by the hydrophobic interaction of alkyl groups with adjacent ones. In the case of the intercalation of surfactant into clay,[13,14] it is generally accepted that C. S. (clearance space = basal spacing ($d_{001}$)-thickness of layer (0.96 nm)) depends on the alkyl chain length, where the alkyl chain conformation of surfactants in the interlayer is presumed to be all-*trans*.[15] The C. S. calculated from XRD is proportional to the length of alkyl groups (Figure 1(B), slope: 0.12 $nm/CH_2$). This result well agrees with the surfactant–clay model.[14]

The transmission electron microscopy (TEM) image for Rh-

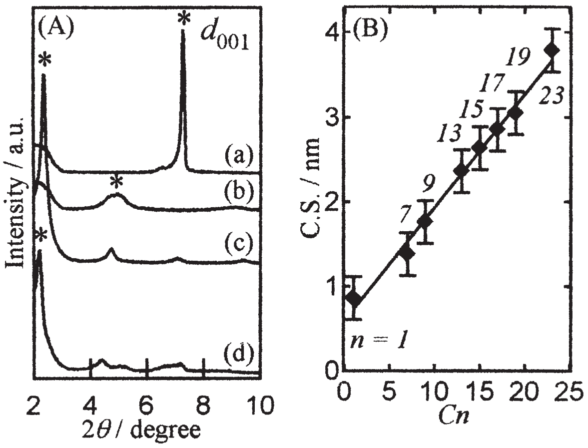

**Figure 1.** (A) XRD patterns of (a) LiTN, (b) Rh-*C1*-bpy/TN, (c) Rh-*C15*-bpy/TN and (d) Rh-*C19*-bpy/TN. (B) The relation between C. S. for Rh-*Cn*-bpy/TN and carbon number (*Cn*) of alkyl groups in *Cn*-bpy.

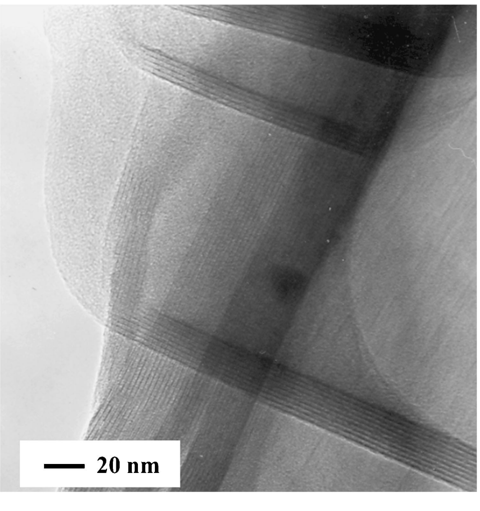

**Figure 2.** TEM image of Rh-*C9*-bpy/TN.

*C9*-bpy/TN is shown in Figure 2. The interlayer space is estimated to be $2.6 \pm 0.2$ nm which is well consistent to the C. S. calculated from XRD.

Solid-state $^{13}$C NMR study for our nano-structured clays was performed to elucidate the conformation of the pillar complexes in the clay (all-*trans* or disordered).[16,17] We measured $^{13}$C CP MAS NMR for *C19*-bpy and Rh-*C19*-bpy/TN (Figure 3). The chemical shift for the main peak of the ligand (*C19*-bpy) was 33.8 ppm (Figure 3a), while the main peak of the ligand in solution ($CDCl_3$) was observed at 29.7 ppm. The lower field shift by 4.1 ppm can be ascribed to a conformational change from disordered to all-*trans* conformation. For Rh-*C19*-bpy/TN, a main peak was observed at 32.9 ppm with a shoulder at 30.7 ppm. (Figure 3b). The peak at 32.9 ppm can be assigned to the alkyl chains with all-*trans* conformation.[18] It can be concluded alkyl chain has all-*trans* conformation to expand the interlayer. However, the spectra in Figure 3b shows shoulder peak at 30.7 ppm, which is assigned to methylene groups in a gauche conformation.[16] It is plausible that one alkyl chain of the ligand has gauche conformation in the alkyl chain.

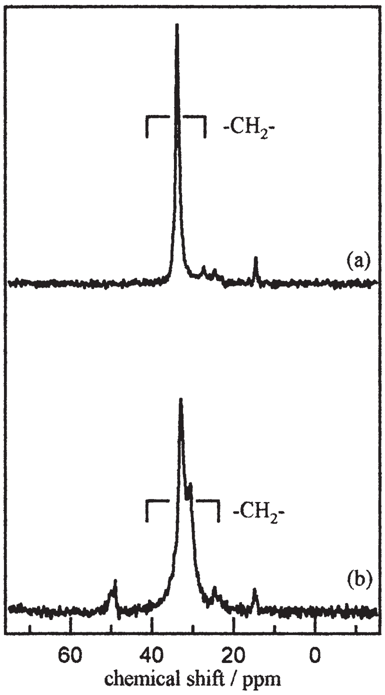

**Figure 3.** $^{13}$C CP MAS NMR spectra of (a) *C19*-bpy (ligand) and (b) Rh-*C19*-bpy/TN swelled with methanol.

CHN analysis showed that the contents of pillar complexes were 50–55-mmol Rh (100 g-clay)$^{-1}$, which corresponded to 30–35% of the cation exchange capacity. Taking account of the clearance space, the loading amounts and the guest molecular size, a suitable conformation of the pillar complexes can be a bilayer arrangement with a tilting angle of ca. 40 degree (Figure 4). In many cases, clays modified with metal complexes show low crystallinity and have monolayer arrangement.[5–7] In contrast, our nano-structured clays show high crystallinity due to the hydrophobic interactions of the alkyl chains. From these results, the bilayer arrangement of the complexes in the layer is the most proper conformation.

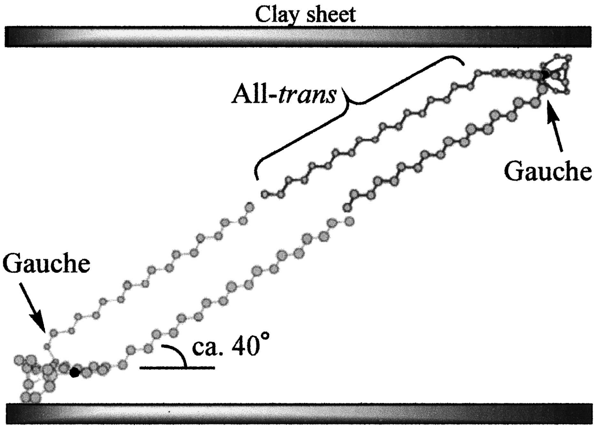

**Figure 4.** Plausible conformation of Rh-*C19*-bpy/TN.

In summary, novel nano-structured clay was prepared by the intercalation. Expansion of C. S. was proportional to the alkyl chain length. Complexes in the interlayer were fixed between the clay sheet and the nano-sized space was constructed. Further studies with catalytic reaction are in progress.

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