Electronic Supplementary Information (ESI)

Inorganic Liquid Crystal Phases in the Aqueous Colloids of Size-Controlled Fluorinated Layered Clay Mineral Nanosheets

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1. Details of the experiment

1.1. Purification of the synthetic clay samples

The clay mineral samples received from Topy Industries Ltd. (Tokyo, Japan) were the aqueous sol (FHT; NHT-sol-B2) or powders (FTSM; DMA-350) and both of them contained certain amount of impurities. These fluorinated clay minerals were synthesized from a molten mixtures of the materials, according to the company. We established very simple and effective procedure to remove most of the impurities in the as-received samples as follows. First, we prepared the clay colloidal sols of ca. 5 wt. % by dispersing the FTSM powder in water or by using the as-received FHT sol. After centrifugation of the sol at 15000 rpm for 1 h, we obtained three phases with clear boundaries: upper supernatant phase, intermediate viscose sol phase, and bottom sediment phase. We finally collected only the intermediate viscose sol phase, which contain 7-10 wt. % of pure clay nanosheets and very small amount of the impurities. The impurities were condensed into the bottom sediment phase. This is confirmed by XRD measurement of the powders recovered from each phases (Fig. S1). After this purification process, about 40-60 wt. % of the starting material is recovered.

1.2. Control of the mean lateral sizes of the nanosheets by ultrasonication.

The control of lateral size of the nanosheets is crucial in investigations of clay colloid. We found very effective way to control the lateral size of niobate nanosheet as reported in the literature (N. Miyamoto and T. Nakato, *J. Phys. Chem. B*, **2004**, *108*, 6152). This methodology is advantageous over other methods such as selection of the nanosheets size only

by centrifugation or controlling particle size of starting material; we can obtain size-controlled nanosheets in very high yield by the very simple and easy procedure.

Here, this methodology was successfully applied to the clay mineral system in the present study. The purified clay colloid was ultrasonicated for 24 h in a conventional ultrasonic cleaner (FU-22H, Fine; 150 W) in a glass vessel. It should be noted that many factors such as the power of ultrasonic, the duration of the sonication, and colloid concentration affect the resulting mean lateral size and polydispersity of the nanosheets. Details are now under investigation.

1.3. Elemental analyses of the purified fluorinated clay minerals

We performed elemental analyses of the purified FHT and FTSM samples, and obtained the results as shown in Table S1. Based on the assumption that the molar ratio of Si over O is 4:1 in general 2:1 type clay minerals such as hectorite and mica, we calculated the chemical compositions as $Na_{0.46}Mg_{2.60}Li_{0.46}Si_4O_{10}F_{2.00}$ and $Na_{0.75}Mg_{2.83}Si_4O_{10}F_{2.13}$ for FHT and FTSM, respectively, from the obtained results.

Table S1 The results of elemental analysis (mass %)

sample	Si	Mg	Li	Na	F
FHT	24.50	13.90	0.70	2.30	8.30
FTSM	24.20	14.80	0.00	3.70	8.70

The evaluated composition of FHT is mostly in accordance with the "ideal" composition ($Na_{0.33}Mg_{2.67}Li_{0.33}Si_4O_{10}F_2$) given by the supplier, Topy Industries Ltd. The result ($Na_{0.46}Mg_{2.60}Li_{0.46}Si_4O_{10}F_{2.00}$) indicates that all of the hydroxy groups are replaced by F atoms as expected. The degree of the isomorphous substitution of Mg^{2+} in the octahedral layer by Li^+ is higher than the ideal value, so that the amount of exchangeable Na in the interlayer space is also larger.

In the case of FTSM, the "ideal" chemical composition given by the supplier is $Na_{1.0}Mg_{2.5}Si_4O_{10}F_2$; it is thought that a part of Mg site is vacant or substituted by Na^+ so that the clay sheet have negative charge compensated by interlayer Na^+, while hydroxy group is fully substituted by F. The evaluated composition ($Na_{0.75}Mg_{2.83}Si_4O_{10}F_{2.13}$) shows some difference in the amount of Mg and Na than expected.

The methods for the elemental analyses are as follows: For the analysis of Si, a powder sample was dissolved in the presence of sodium carbonate and boric acid. For analysis of Li, Na, and Mg elements, a powder sample was dissolved in the presence of hydrofluoric acid and sulfuric acid. For the analysis of F element, a powder sample was dissolved in the presence of sodium peroxide. Si and Mg were analyzed with inductively coupled plasma atomic emission spectroscopy (Seiko Instruments Inc. SPS1700HVR). Varian Spectra AA-20 atomic absorption spectrometer was used for the analyses of Li and Na. F element was analyzed by lanthanum/alizarin complexone method, by using JASCO Ubest-35 spectrometer.

2. Supporting Figures

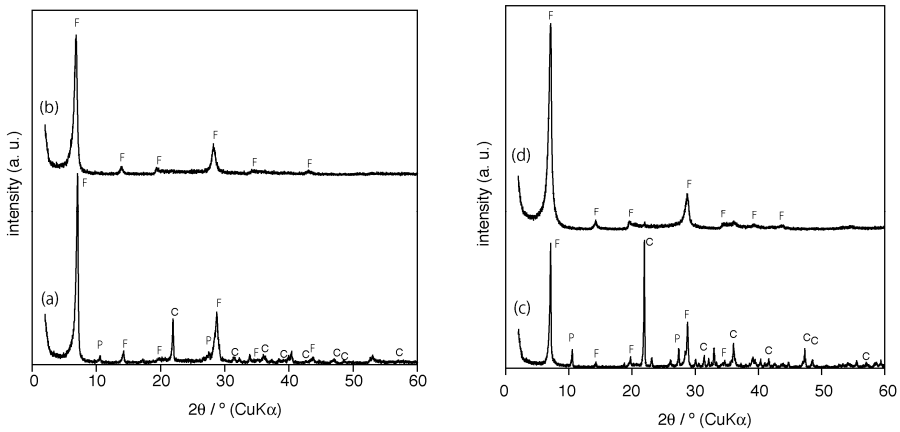

Fig. S1. XRD patterns of (a) purified FHT, (b) the precipitate removed by centrifugation of FHT, (c) purified FTSM, (d) the precipitate removed by centrifugation of FTSM. The peaks marked as F, T, P, and C are ascribed to fluorohectorite, fluortetrasilisic mica, protoamphibole, and cristobalite, respectively. It is confirmed that only trace amount of impurity remains after the purification.

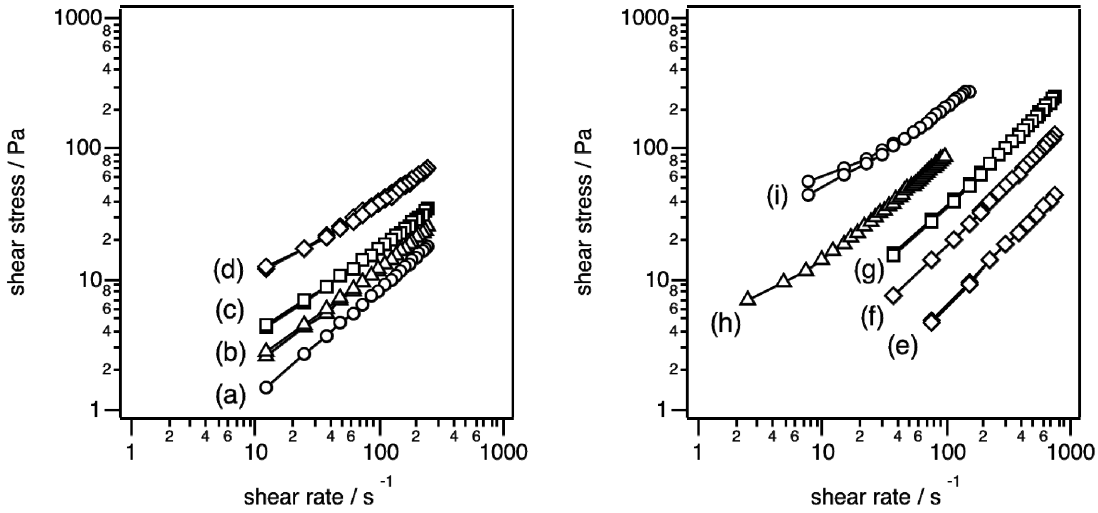

Fig. S2. Flow-curves of (a)-(d) FHT and (e)-(i) FTSM colloids. The concentrations are (a) 3, (b) 4, (c) 5, and (d) 7 wt. % for FHT systems, and (e) 1, (f) 2, (g) 3, (h) 5, and (i) 6 wt. % for FTSM systems. The curves indicate that most of the colloids show Newtonian or weak pseudo-plastic flow behavior. In the FTSM colloids of 5 and 7 wt. %, the curves are characteristic to Bingham liquids, indicating they are weak physical gels. In all the concentration range, the shear stresses are larger for FHT than FTSM, showing that FHT colloids are more viscose than FTSM.