Electronic Supplementary Information (ESI)

Liquid Crystalline Inorganic Nanosheets for Facile Synthesis of Hydrogels with Anisotropies in Structure, Swell/Deswelling, and Ion Transport/Fixation

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1. Experiment procedures

Liquid crystalline colloidal dispersion of the inorganic nanosheets fluorohectorite (FHT) was obtained by purification of NHT-SOL donated from Topy Industries Ltd., Tokyo, Japan, according to the method we recently published (Miyamoto, N., Iijima, H., Ohkubo, H. & Yamauchi, Y. *Chem. Commun*. **46**, 4166-4168 (2010)). FHT is a layered clay mineral with the chemical composition of $Na_{0.46}[Mg_{2.60}Li_{0.46}Si_4O_{10}F_{2.00}]$ where Na is the exchangeable counter cation. The FHT nanosheets obtained by exfoliation of fluorohectorite in this study have average lateral size of 2.2 μm and the thickness of 0.9 nm as observed by transmission electron micrography. The schematic drawing of the formation of liquid crystal phase of inorganic nanosheet colloid by exfoliation of FHT is shown in Scheme S1 with the schematic structure of FHT.

N-isopropylacrylamide (NIPA) was recrystallized from hexane and acetone. Ammoniumperoxide disulfate (APS; initiator), N,N,N',N'-tetramethylethylenediamine (TEMED; initiation accelerator), and N,N'-methylenebisacrylamide (BIS; chemical crosslinker), and the dyes (1,1'-diethyl-2,2'-cyanine iodide and Rhodamine 6G chloride) were used without purification.

In a typical synthesis of the gel, NIPA monomer (6.5 mmol), FHT (0.5 g), and BIS (0.065☐mol) were dissolved in water (10 g) and bubbled with N_2, followed by addition of APS (0.1 mmol) and TEMED (0.1 mmol) to initiate radical polymerization in glass tubes for 2 days at 20 ºC. The obtained gels were stored in distilled water for a week to remove unreacted monomers and to swell the gel to the equilibrium state. The water content in the fully swollen gel was determined by comparing the weights of fully swollen gel and the gel dried in an oven at 90 ºC for 36 h. We name the gels as Fx-By-gel, where x and y are the concentrations (wt. %) of FHT and BIS in the initial reaction mixture. The gels were adsorbed with the cationic dyes by immersing a gel in the solutions of the dyes.

The birefringence of the gels was measured with a Bereck compensator. The photographic images of the gels were taken with a digital camera by using the crossed polarizer/analyzer and the wave plate (the retardation of the wave plate is 530 nm) to check the macroscopic orientation of the birefringent domains on cm scale.

Small angle X-ray scattering (SAXS) measurements were performed on Rigaku Nano-Viewer (CuK☐-radiation) equipped with a 2D-CCD detector, using a 2 mm-thick cell sealed with an O-ring and a Capton film window (75☐m thick). The use of this cell allows us in-situ observation of the polymerization process under N_2 atmosphere. For the in-situ observation, the reaction mixture prepared under N_2 atmosphere was injected into the N_2-purged cell, immediately after the initiation of the reaction (addition of TEMED). The mixture was injected by using a syringe with a needle without contact to air. The needle was removed after the injection. Then, the SAXS measurements were performed with the interval of 1 minute. After the completion of the synthesis, swelling process was observed. The synthesized gel was stored in pure water for certain period, taken out from the water, put into the cell, and measured by SAXS; this cycle was repeated several times.
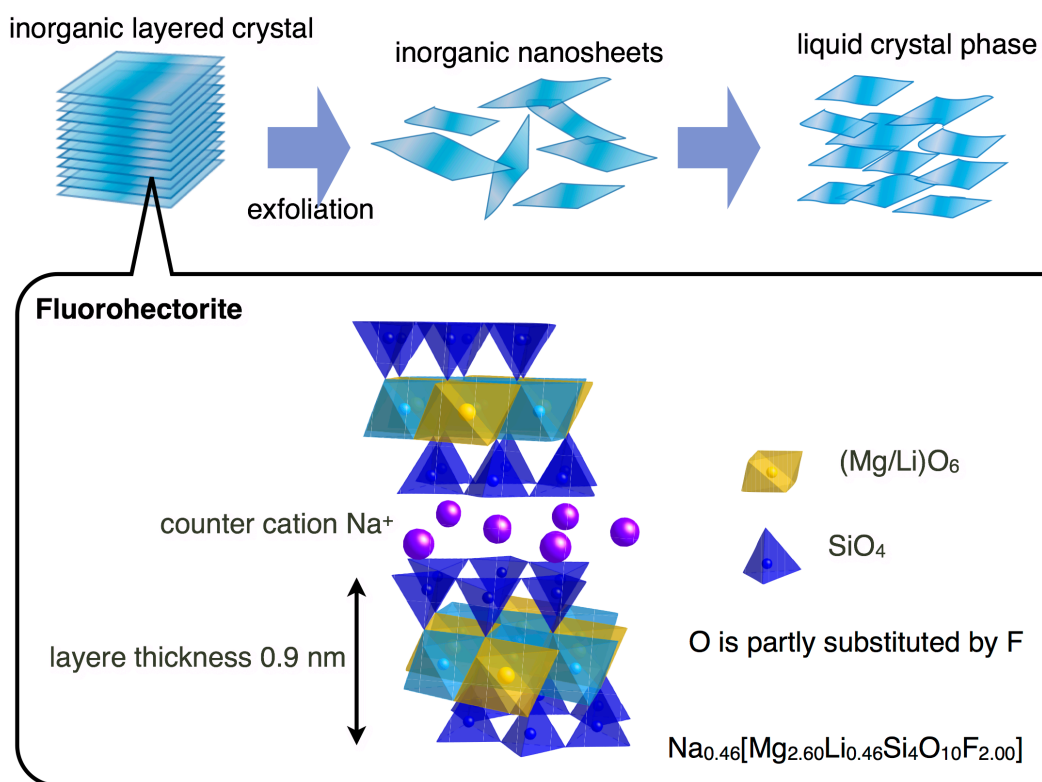
The measured raw data of 2D SAXS were corrected for measurement time, transmittance of X-ray beam, and background scattering (water in the cell), followed by

circularly averaging to obtain $I(q)$ *vs* q plots (1D SAXS profiles) where q is the magnitude of the scattering vector. Because the observed $I(q)$ is the product of the structure factor $S(q)$ and the form factor $P(q)$, and the form factor of the nanosheets is $P(q) \sim q^{-2}$ in the measured q-range, the structure factor $S(q)$ is calculated as $S(q) = I(q)\, q^2$. Thus, the SAXS data is finally converted to $I(q)\, q^2$ *vs* q plot to clearly distinguish the structure factor.

The thermally induced volume phase transition behaviors of the gels were evaluated as follows. The cylindrical gel synthesized in a glass capillary with the diameter of 0.63 mm is placed in a glass cell filled with water and sealed with silicon rubber. The cell is placed in a water bath with controlled temperature for at least 10 min. The cell is then taken from the bath and placed on the stage of polarized optical microscopy (Olympus BX51) for the observation with crossed polarizer/analyzer. After the observation, the cell is placed into the bath again. This cycle was repeated. The temperature is set as 20 ℃ for the first observation and is increased by 1℃ until it reaches 40 ℃.

The mechanical strength of the gel was evaluated by the compression test by using Orientec STA-1150 at the compression rate of 3 mm min^{-1}.

2. Supporting Schemes and Figures

inorganic layered crystal

inorganic nanosheets

liquid crystal phase

exfoliation

Fluorohectorite

counter cation Na+

$(Mg/Li)O_6$

SiO_4

layere thickness 0.9 nm

O is partly substituted by F

$Na_{0.46}[Mg_{2.60}Li_{0.46}Si_4O_{10}F_{2.00}]$

Scheme S1. The schematic drawing of the formation of liquid crystal phase of inorganic nanosheet colloid by exfoliation of inorganic layered crystal. The schematic structure and the chemical composition of the fluorohectorite are also shown.
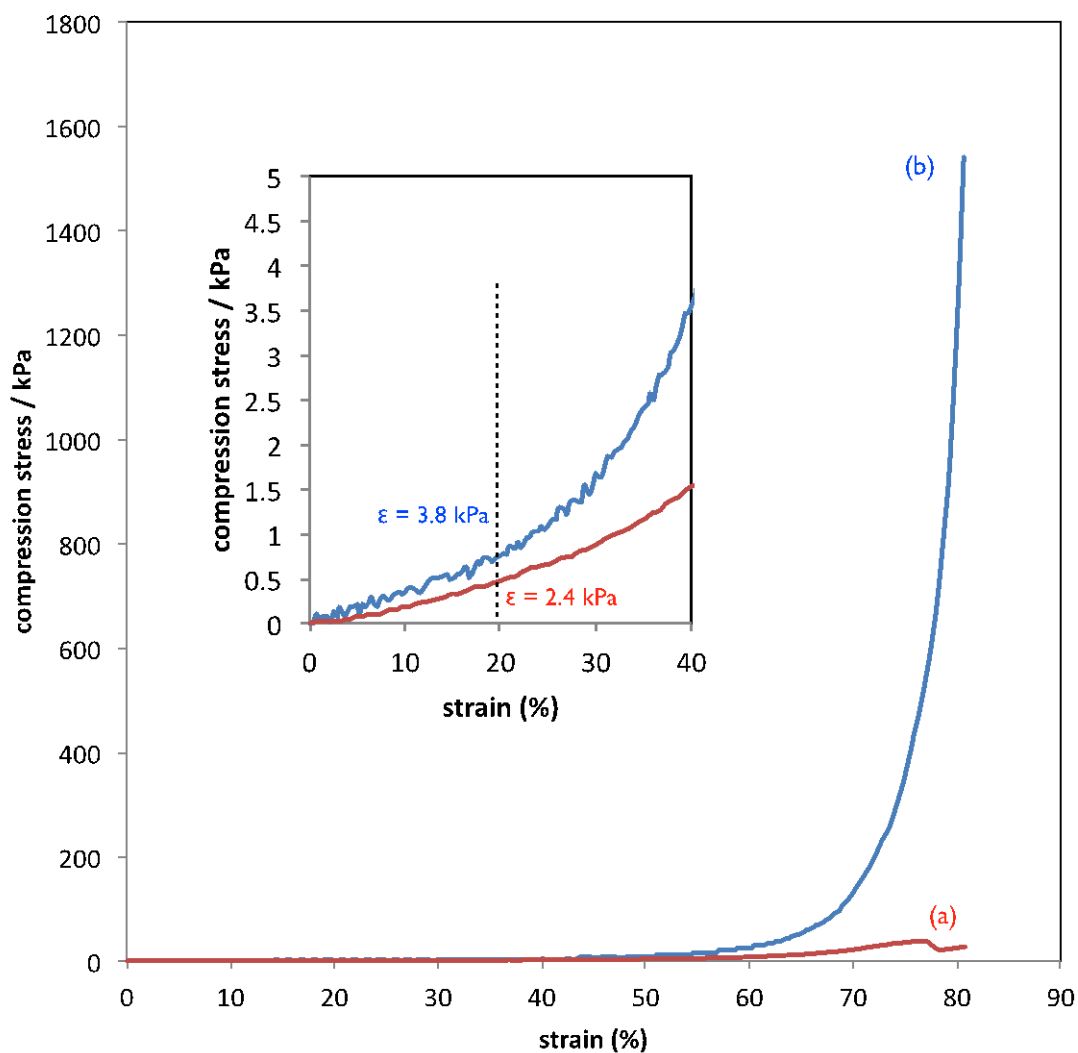
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Fig S1. The stress-strain curves for the (a) F0-B0.1-gel and (b) F5-B0.1-gel as evaluated by the compression test. The inset is the enlarged view at small strain region. The Compression modulus ε is evaluated from the stress at the strain of 20 % and shown in the figure. The gel hybridized with FHT (F5-B0.1-gel) is compressed without a fracture even at the strain of 80 % and the stress of 1.5 MPa, while the gel without FHT fractures at the strain of 75 %.
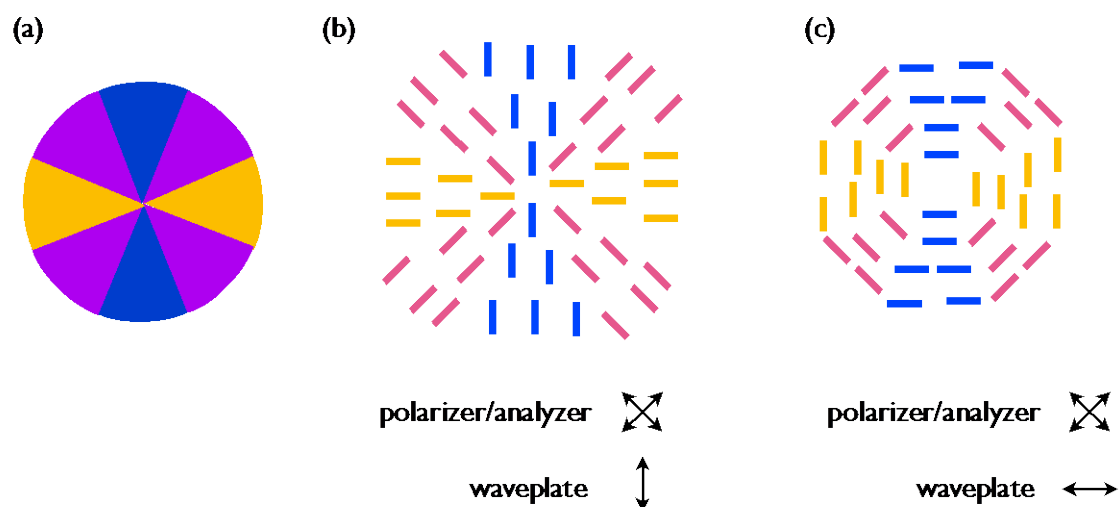
Fig S2. Schematic explanation for the observation of a birefringent concentric or spray structure samples by using crossed polarizer/analyzer and a wave plate. If we observe a sliced cylinder sample with a small retardation Δ, using a crossed polarizer/analyzer and a wave plate, we may obtain the image like (a). For this image, two possible orientations of the birefringent domains is considered. One is the spray type (b) and the other is the concentric (tree-ring) type (c). We distinguish the two possible orientations as follows. Generally, if the direction of the birefringent domain is parallel and perpendicular to the direction of the waveplate, the retardation of the sample Δ is added to or subtracted from that of the waveplate (530 nm), respectively. The interference colors are observed as blue, purple, and yellow for the retardation of $530 + \Delta$ nm, 530 nm, and $530 - \Delta$ nm, respectively. Therefore, in the case that the image like (a) is obtained with the vertical waveplate direction like (b), we confirm the spray type orientation. If the direction of the waveplate is horizontal like (c), the orientation is tree-ring type.
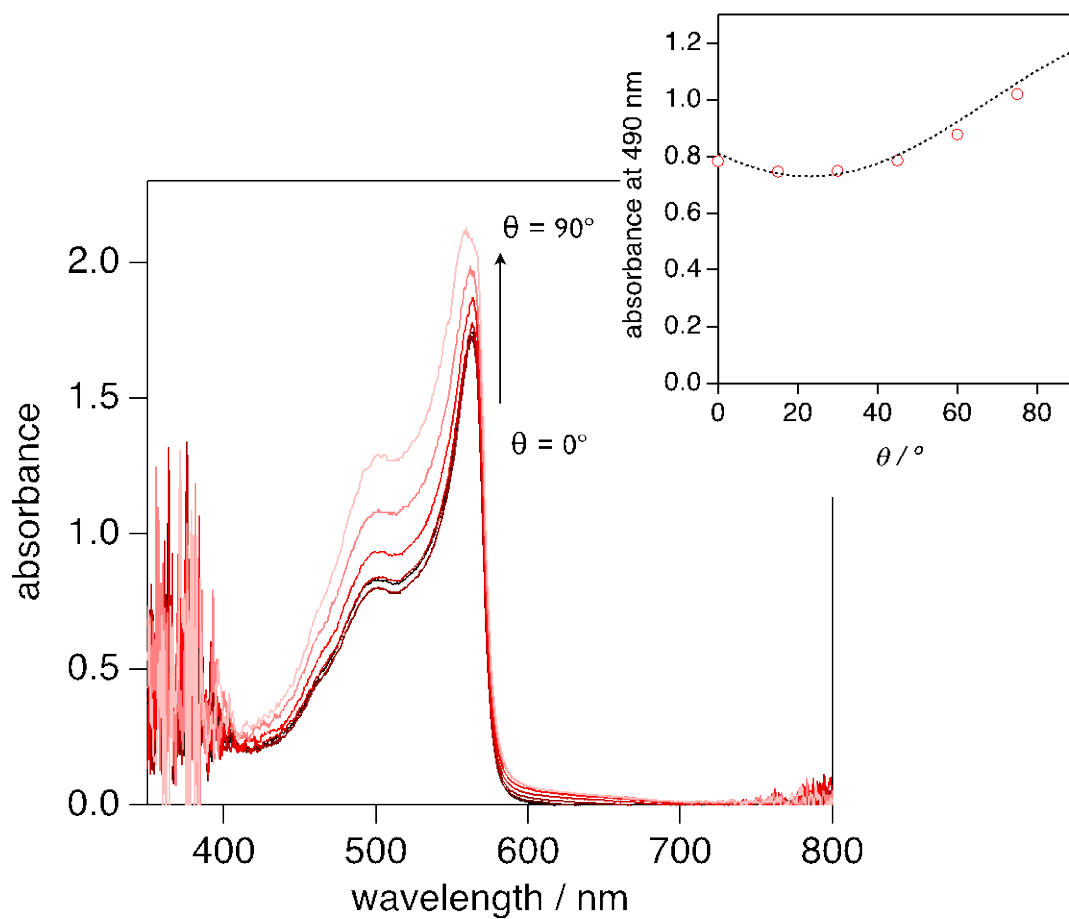
Fig S3. The polarized visible absorption spectra of the F0-B0.1-gel adsorbed with the cyanine dye. The angle θ between the polarizer and the longer axis of the gel was set to 0, 15, 30, 45, 60, 75, and 90º. In the inset, the absorbance at 490 nm is plotted against the angle θ, the dotted line is the curve fitted to the equation $A\sin^2(\theta - B) + C$.
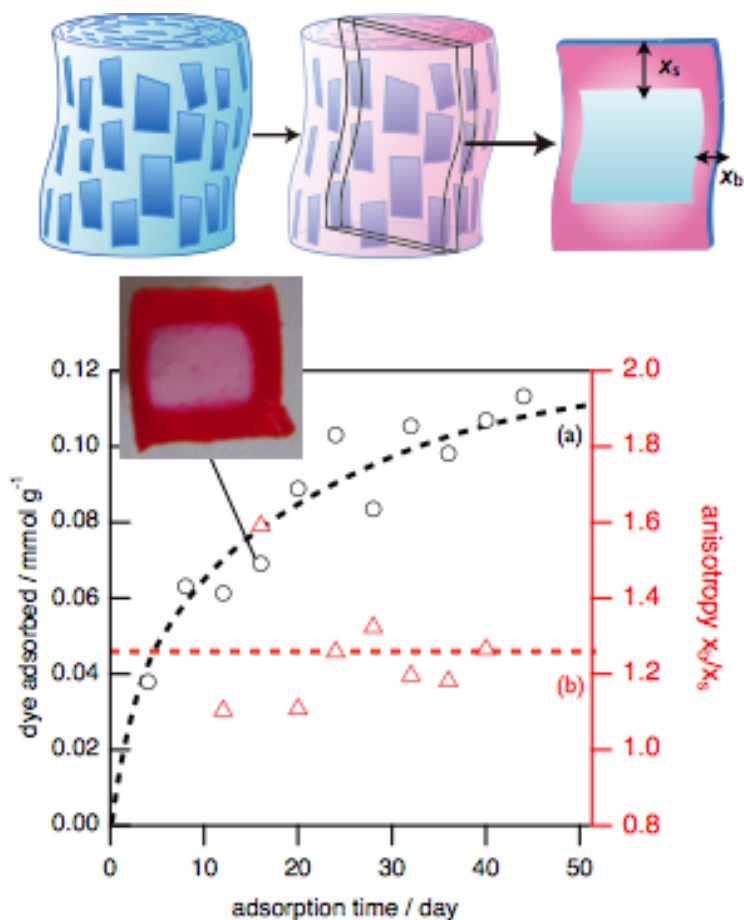
Fig S4. The anisotropic uptake of a cationic dye Rhodamine 6G to the F5-B0.1-gel. The cylindrical gel (5 mm in diameter and 5 mm in height) was immersed in the aqueous solution of the dye at room temperature and the amount of the adsorbed dye was monitored by UV-visible spectrum. The anisotropic uptake of the dye was evaluated as follows: after immersing the gel in the dye solution, the gel was sliced as in the manner shown in the top cartoon. We performed experiments with 11 batches by using 11 gels with mostly the same size and shape by changing only the adsorption time to obtain the data of (a) adsorbed amount of the dye and (b) the anisotropy as the function of time. As shown in the inset photograph, the length of colored domain along the bottom edge (x_b) is longer than that along the side edge of the cylinder (x_s). The anisotropy x_b/x_s is shown as plot (b) and the average value of 1.3 is obtained, indicating the faster diffusion of the dye from the bottom edge than from the side edge. Although the data are collected from different batches, anisotropy x_b/x_s always keep larger than 1, confirming the reproducibility of this experiment.