

Supporting Information

π - π Interaction-induced Vertical Alignment of Silica Mesochannels Templated by a Discotic Lyotropic Liquid Crystal

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Materials

2,3,6,7,10,11-Hexa-(1,4,7-trioxaoctyl)triphenylene, abbreviated as TP6EO2M, was synthesized by Williamson-ether reaction from 2,3,6,7,10,11-hexahydroxytriphenylene. The details of the synthesis of this compound were described in the previous literatures.^{1,2} 2,4,7-Trinitro-9-fluorenone (TNF) was purchased from TCI. Charge-transfer (CT) complex was prepared by mixing TP6EO2M with TNF (molar ratio of 1.5: 1), followed by annealing at ca. 170 °C. The CT complex/silica hybrid films were prepared from a silica sol solution containing the CT complex as described below. Columnar aggregates formed by pure TP6EO2M were not stable enough to conduct this work, therefore the more thermally stable CT complex was used in this study. Tetraethoxysilane (TEOS), ethanol (EtOH), and hydrochloric acid (HCl) were purchased from Kanto Chemical Co. TNF, TEOS, EtOH, and HCl were used without further purification. Pure water (Milli-Q grade, 18 M Ω cm) was used to prepare the silica sol solution.

Measurements

X-ray diffraction (XRD) measurements for evaluation of lyotropic liquid crystallinity of bulk were performed on an FR-E (Rigaku) diffractometer using Cu K α radiation (0.154 nm) with an imaging plate (IP) detector. Alignment of mesostructure in the LCs/silica hybrid films were characterized by grazing-incidence XRD (GI-XRD) measurements. The GI attachment was placed on the FR-E equipment. Field-emission transmission electron microscopy (FE-TEM) observations were performed with a JEM-2200FS (JEOL). Fourier transform infrared (FT-IR) spectra were recorded on a Bio Rad FTS 6000 spectrometer.

Structural characterization of the CT complex.

We measure lyotropic liquid crystallinity of the CT complex in a sol solution. Figure S1 shows XRD profile of 50 wt% CT complex-sol solution at room temperature (r.t.). Sharp peaks were observed at 4.1 ° and 26.2 °, which were equal to periodic structures of 2.2 nm and 0.3 nm, respectively. The spacing of ca. 2 nm is a characteristic diffraction for hexagonal columnar structure of the CT complex.³ A diffraction corresponding to 0.3 nm can be assignable to a π stacking of the CT complex.³ We can recognize from these facts that the CT complex exhibits lyotropic liquid crystallinity in sol solution as that in water.

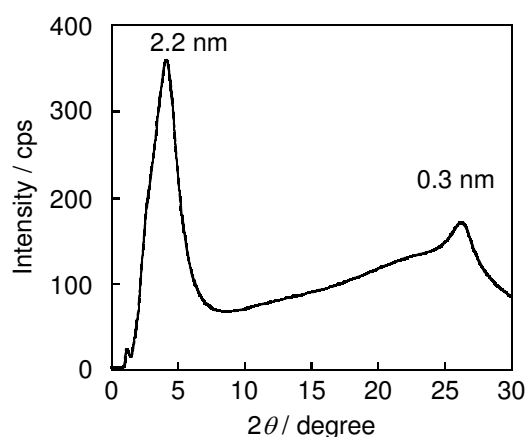


Figure S1. XRD pattern of 50 wt% TP6EO2M aqueous solution.

Orientation of the hexagonal column array on silicon wafer.

The CT complex/silica hybrid films were prepared onto various surface-energy Si wafers by the same deposition method as described above. Hydrophilic and hydrophobic Si wafers were prepared according to the following procedures. The contact angle of water on the silicon wafer surface without treatment was ca. 50 ° (Figure S2(b)). The silicon wafers cleaned by UV/O₃ treatment became highly hydrophilic with a water-contact angle of ca. 5 ° (a). Then one of the cleaned Si wafers were immersed into 0.9 wt% octadecyldimethylchlorosilane (ODDS)-toluene solution containing 0.4 wt% conc. HCl as a promoter for 1 day, then dipped into ethanol successively and washed by ultrasonic bath for 30 min. The resulting hydrophobilized substrate exhibited a water-contact angle of ca. 105 ° (c).

In the case of the films deposited onto the Si wafers, three spots with a spacing period of ca. 2 nm ($2\theta = 3.8^\circ$) were observed to the out-of-plane direction of the films in the GI-XRD images in all of the Si wafers with various surface energies (Figure S2). According to the graph, these peaks were attributed to the (1 0), (0 1), and (-1 1) diffractions of hexagonal-packed columnar structure that aligned to the parallel to the substrate plane. In the entire hybrid films deposited onto the Si wafers, alignment of the columnar structure was parallel to the substrate plane independent of the surface energy.

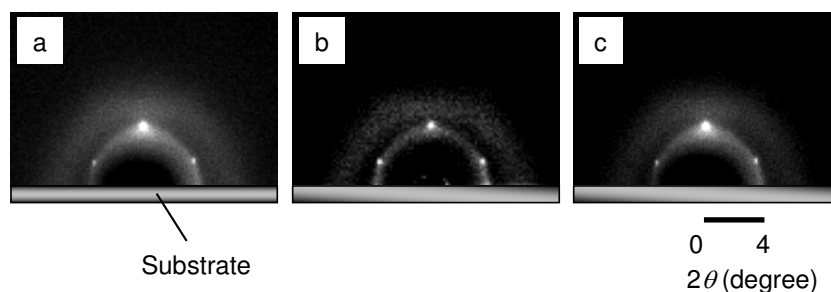


Figure S2. Diffraction patterns on the imaging plates obtained by GI-XRD measurements of the CT complex/silica hybrid films deposited onto UV/O₃ cleaned Si wafer (a), non-treated Si wafer (b), and ODDS-modified Si wafer (c) at 40 °C for 12 h.

Silylation reaction before the calcination.

The silica network was reinforced by further silylation with dichlorodimethylsilane. The proceeding of this reaction in the hybrid film was studied by IR measurements (Figure S3). As the reaction proceeded, the absorption intensities at 806 cm^{-1} ($\text{CH}_3\text{-Si-CH}_3$ symmetric deformation), 1265 cm^{-1} ($\text{CH}_3\text{-Si-CH}_3$ symmetric deformation), and 2965 cm^{-1} (CH_3 asymmetric stretch) increased and those at 958 cm^{-1} (CH_3 rocking vibration from TEOS), 1135 cm^{-1} (CH_3 rocking vibration from TEOS), and 3300 cm^{-1} (Si-OH asymmetric stretch from TEOS) decreased, respectively.⁴

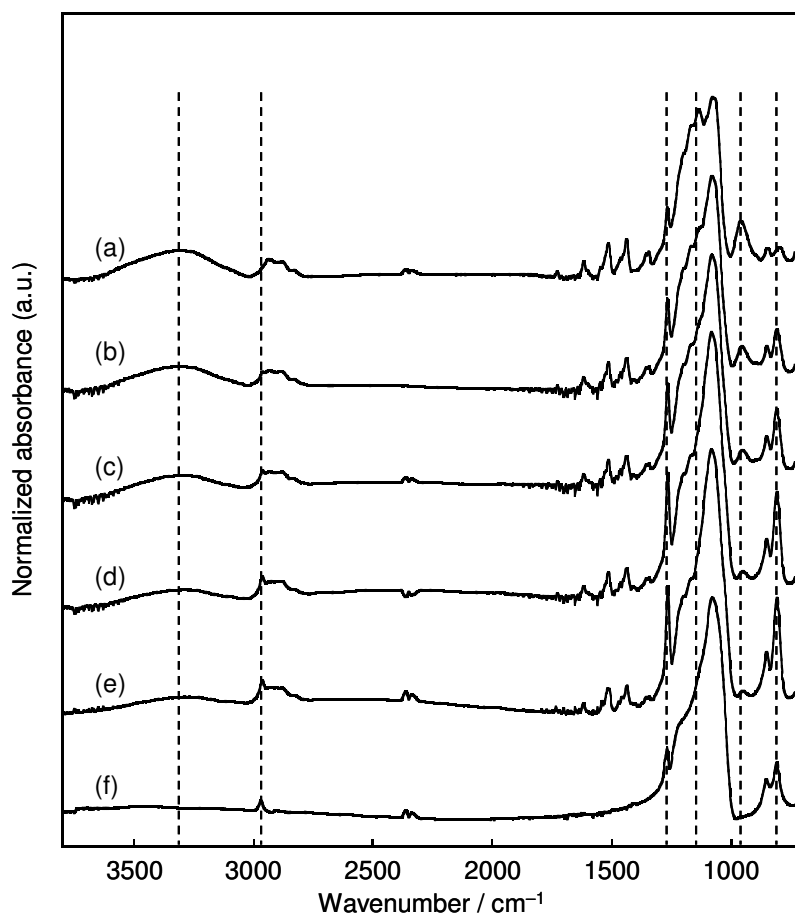


Figure S3. IR spectra of the CT complex/silica hybrid films deposited onto Si wafers at $20\text{ }^{\circ}\text{C}$ for 96 h (a), silylated of the as-synthesized hybrid films for 1 h (b), 2 h (c), 15 h (d), 30 h (e), and calcinated at $400\text{ }^{\circ}\text{C}$ for 1 h of the hybrid films silylated for 30 h (f).

References

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