Organic-Inorganic Hybrid Liquid Crystals: Hybridization of Calamitic Liquid-Crystalline Amines with Monodispersed Anisotropic TiO_2 Nanoparticles

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Supporting Information

1. General.

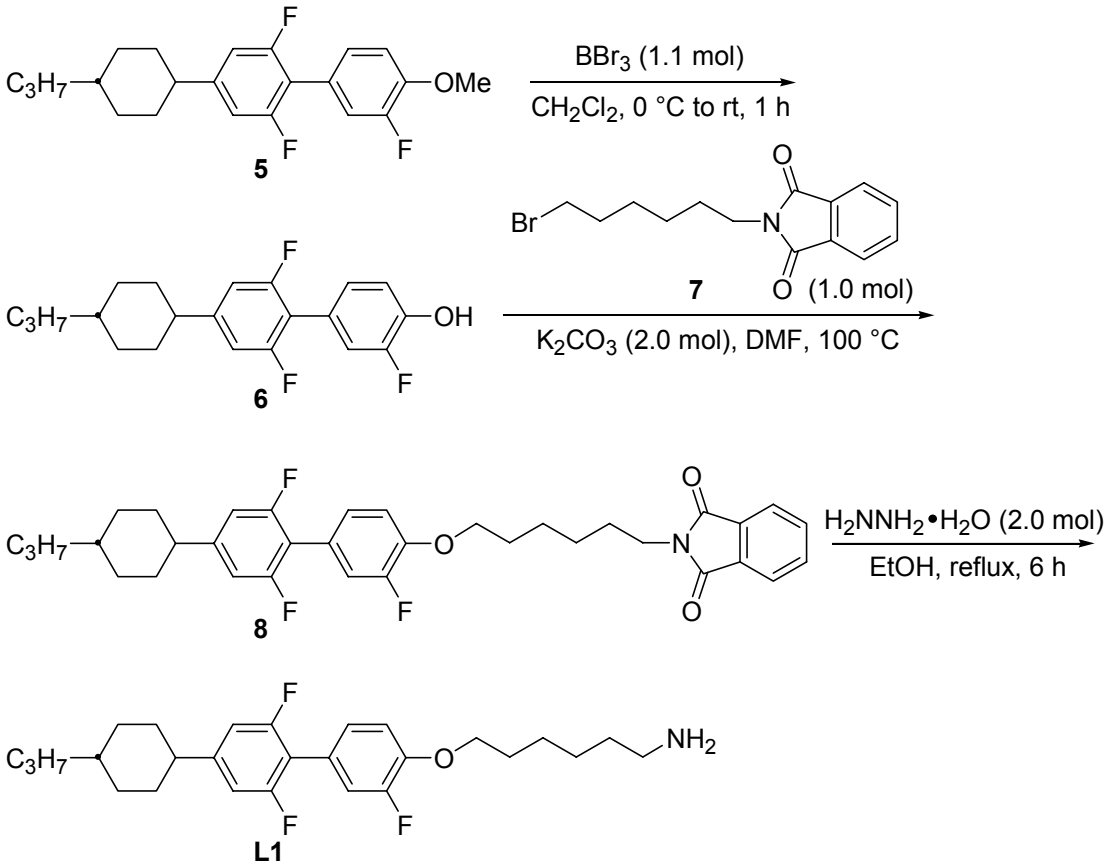
All reagents of the highest commercial quality and solvents were purchased from Aldrich Chemicals, Wako Pure Chemicals, Nakalai Tesque, Kanto Chemicals, or Tokyo Kasei, and were used as received. Water was doubly distilled and deionized prior to use. Titanium (IV) tetraisopropoxide (TIPO, 5N) purchased form Kojundo Chemical Laboratory Co., Ltd was used for the preparation of TiO_2 particles. All of the organic reactions were carried out under an argon atmosphere in a dry solvent purchased from Wako Pure Chemicals or Kanto Chemicals. Glass vessels for the organic reactions were well-dried by heating under reduced pressure. Silica gel from Kanto Chemicals (Silica Gel 60, Spherical, 63-210 μm, Neutral) was used for column chromatography. Measurements of phase transition temperatures and determinations of liquid-crystalline phases were carried out with an Olympus BX51 optical polarizing microscope equipped with a Mettler FP82 HT hot stage. Thermal characterization was performed with a TA Instruments MDSC 2920 equipped with a cooling can. The scanning rate was 10 °C/min. Infrared (IR) spectra were conducted on a Bio-Rad FTS-40A equipped with a microscope. IR measurements for characterization of molecules were carried out by making KBr pellets. Variable-temperature IR spectra were recorded on the microscope

equipped with a hot stage. Samples were sandwiched with a couple of KBr plate-like crystals for the measurements. NMR spectra were measured in a $CDCl_3$ solution. ^1H NMR spectra were recorded on a JEOL JNM-LA400. Chemical shifts of ^1H NMR signals were quoted to internal standard Me_4Si ($\delta = 0.00$) and expressed as chemical shifts in ppm (δ), multiplicity, coupling constant (Hz), and relative intensity. Mass spectra were recorded on a Bruker FT-MS APEXIII spectrometer (70 eV). Wide angle X-ray diffraction (WAXD) measurements were carried out on a Rigaku RAD-B system using Ni-filtered CuKα radiation (36 kV, 20 mA). Variable-temperature WAXD profiles were recorded on a Rigaku RINT-H system with a heating stage using a CuKα beam (50 kV, 32 mA). Temperature variable small angle X-ray scattering (SAXS) measurements were carried out by using a custom-built apparatus. An 18 kW rotating-anode X-ray generator, a Rigaku ultraX 18, was mounted on the custom set-up. Transition electron microscopic (TEM) observations were performed by using a JEM-1200EX II with an acceleration voltage of 120 kV. Surface area measurements of TiO_2 particles were performed on Shimadzu Micromeritics Automatic Surface Area Analyzer Gemini by using nitrogen adsorption (BET method). X-ray photoelectron spectroscopic (XPS) observations were carried out by PHI 5600 ESCA system using MgKα radiation.

2. Synthesis of Organic Molecules

2-1. Preparation of 6-[3,2',6'-Trifluoro-4'-(*trans*-4-propylcyclohexyl)biphenyl-4-yloxy]hexylamine (L1).

Preparation of **L1** was carried out by the route as shown in Scheme S1.



Scheme S1. Synthesis of Mesogenic Molecule **L1** wih an amino group.

The procedure is as follows: A dichloromethane (20 mL) solution of 2,6,3'-trifluoro-4'-methoxy-4-(*trans*-4-propylcyclohexyl)biphenyl (**5**) (3.9 g, 10.8 mmol) was added dropwise a dichloromethane solution of BBr_3 (1.0 M, 12.0 mL, 12.0 mmol) at 0 °C over 10 min with stirring. The resulting light brown solution was allowed to warm to room temperature over 30 min, and stirred at the temperature for 1 h. Isopropanol (3 mL) and water (5 mL) were slowly added dropwise into the reaction solution, successively, to destroy the excess of BBr_3. The resulting mixture was poured into a separation funnel containing $CHCl_3$ (200 mL) and water (200 mL). The organic

phase was separated, and the aqueous phase was extracted three times with $CHCl_3$ (total, 300 mL). The combined organic extracts were washed with a sat aqueous NaCl solution, dried over anhydrous $MgSO_4$, filtered through a pad of Celite, and concentrated under reduced pressure to obtain 2,6,3'-trifluoro-4'-hydroxy-4-(*trans*-4-propylcyclohexyl) biphenyl (**6**) (3.8 g, 10.8 mmol) in a quantitative yield. Further purification was not necessary for the next step. A two-necked round-bottom flask with a magnetic stirring bar was charged with compound **6** (3.8 g, 10.8 mmol), *N*-6-bromopropylphthalimide (**7**) (3.09 g, 10.0 mmol), K_2CO_3 (3.0 g, 20 mmol), and DMF (50 mL). The suspension was heated at 100 °C for 10 h with stirring, and the resulting mixture was poured into a separation funnel containing ethyl acetate (100 mL), $CHCl_3$ (100 mL), and water (200 mL). The organic phase was separated, and the aqueous phase was extracted three times with ethyl acetate (total, 300 mL). The organic extracts were combined and washed with two times with saturated NH_4Cl aqueous solution. The resulting organic phase was dried over $MgSO_4$, filtered, and concentrated *in vacuo*. Recrystallization of the residue from hexane afforded *N*-{6-[3,2',6'-trifluoro-4'-(*trans*-4-propylcyclohexyl)biphenyl-4-yloxy] hexyl}phthalimide (**8**) in a yield of 74% (4.30 g, 7.4 mmol) as a white solid.

A boiling ethanolic suspension (30 mL) of compound **8** (3.03 g, 5.2 mmol) was slowly added dropwise hydrazine monohydrate (0.52 mL, 10.4 mmol) over 10 min with stirring. Among the resulting suspension was heated at reflux for 6 h, the suspension became once colorless solution, and white precipitates were observed. After the volatile components were removed under reduced pressure, the residue was dissolved in water (200 m), $CHCl_3$ (200 mL), and MeOH (5 mL). The resulting mixture was transferred into a separation funnel. The organic phase was separated, and the aqueous phase was extracted three times with $CHCl_3$ (total, 300 mL). The organic extracts were combined and washed with sat. NaCl aqueous solution. The organic phase was dried over anhydrous Na_2SO_4, filtered through a pad of Celite, and concentrated. The residue was purified by column chromatography on Silica gel (eluent: $CHCl_3$; $CHCl_3$-MeOH = 5 : 1 to 3 : 1) to give **L1** in a yield of 88% (2.2 g, 4.6 mmol).

Compound **8**: $C_{35}H_{35}D_3F_3NO_3$. Melting point: 98 °C (DSC on heating). R_f = 0.32 (hexane-EtOAc = 5 : 1). IR 2944, 2913, 2859, 1773, 1709, 1523, 1398, 1358, 1188, 1135, 1048, 1017, 889, 720 cm^{-1}; ^1H NMR (400 MHz) δ = 7.84 (dd, *J* = 3, 6 Hz, 2 H), 7.71 (dd, *J* = 3, 6 Hz, 2 H), 7.19 (d, *J* = 12 Hz, 1 H), 7.15 (d, *J* = 9 Hz, 1 H), 6.99 (dd, *J* = 9, 9 Hz, 1 H), 6.81 (d, *J* = 9 Hz, 2 H), 4.05 (t, *J* = 6 Hz, 2 H), 3.71 (t, *J* = 7 Hz, 2 H), 2.37-2.40 (m, 1 H), 1.92-1.98 (m, 5 H), 1.82-1.91 (m, 2 H), 1.79-1.84 (m, 2 H), 1.66-1.78 (m, 7 H), 1.58-1.64 (m, 2 H), 0.90 (t, *J* = 7 Hz, 3 H); MS (20 eV) *m/z* (rel intensity) 581 (M^++1, 0.17), 580 (M^+, 0.45), 579 (M^+-1, 0.27), 578 (0.15), 353 (1), 352 (7), 351 (24), 350 (18), 252 (14), 251 (29), 250 (10), 231 (15), 230 (100), and 160 (23). Found: *m/z* 580.2987. Calcd for $C_{35}H_{35}D_3F_3NO_3$: M, 580.2989.

Compound **L1**: $C_{27}H_{33}D_3F_3NO$. Phase transition temperature (°C): Cr 35 S_X 73 N 101 Iso (DSC on heating); R_f = 0.76 ($CHCl_3$-MeOH = 5 : 1). IR 3353, 3280, 2927, 2863, 1571, 1532, 1423, 1311, 1240, 1189, 1139, 1020, 888, 848, 746 cm^{-1}; ^1H NMR (400 MHz) δ = 8.29 (brs, 2 H), 7.18 (d, *J* = 12 Hz, 1 H), 7.13 (d, *J* = 8 Hz, 1 H), 6.97 (dd, *J* = 9, 9 Hz, 1 H), 6.82 (d, *J* = 8 Hz, 2 H), 4.03 (t, *J* = 6 Hz, 2 H), 2.96-3.04 (m, 2 H), 2.39-2.48 (m, 1 H), 1.75-1.94 (m, 6 H), 1.44-1.58 (m, 4 H), 1.15-1.42 (m, 6 H), 0.92-1.08 (m, 2 H), 0.90 (t, *J* = 7 Hz, 3 H); MS *m/z* (rel intensity) 451 (M^++1, 2), 450 (M^+, 2), 449 (M^+-1, 1), 352 (3), 351 (11), 350 (9), 252 (24), 251 (48), 250 (18), 195 (21), 140 (22), 100 (100), 98 (33), and 87 (32). Found: *m/z* 450.2922. Calcd for $C_{27}H_{33}D_3F_3NO$: M, 450.2934.

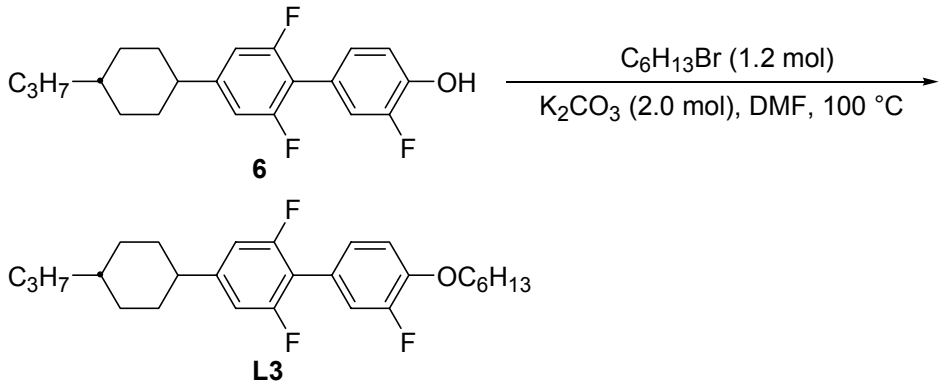
A part of hydrogens on the 2,6-positions of the cyclohexane ring of ***5*** *were substituted by deuteriums. The average number of the substitution is three. Therefore, compounds* ***L1****,* ***L3****,* ***6****, and* ***8*** *also contain about three deuteriums in the molecules.*

2-2. Preparation of 4-(6-aminohexyloxy)-4'-cyanobiphenyl (L2).

Synthesis of **L2** was carried out by the same way for the preparation of **1** starting from 4-cyano-4'-hydroxybiphenyl. Spectra data of **L2** were listed in Chien, L. C.; Cada, L. G.; Xie, L. *Liq. Cryst.* **1992**, *12*, 853.

2-3. Synthesis of 2,6,3'-trifluoro-4'-hexyloxy-4-(*trans*-4-propylcyclohexyl)biphenyl (L3).

Compound **L3** was prepared by the route as shown in Scheme S2.



Scheme S2. Synthesis of Mesogenic Molecule **L3**.

A DMF (20 mL) suspension of compound **6** (1.80 g, 5.0 mmol), 1-bromohexane (0.90 mL, 6.0 mmol), and K_2CO_3 (1.80 g, 12 mmol) was stirred at 100 °C for 10 h. The resulting mixture was poured into a separation funnel containing 200 mL of water and 200 mL of EtOAc. The organic phase was separated, and the aqueous phase was extracted three times with EtOAc (total 300 mL). The combined organic extracts were washed with two times with saturated NH_4Cl aqueous solution. The resulting organic phase was dried over anhydrous $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography on Silica gel to obtain **L2** (1.92 g, 4.45 mmol) in 89% yield.

Compound **L3**: $C_{27}H_{32}D_3F_3O$. Phase transition temperature (°C): Cr 58 S_X 64 N 100 Iso (DSC on heating); R_f = 0.61 (hexane-EtOAc = 10 : 1). IR 2959, 2912, 2856, 1639, 1480, 1417, 1300, 1235, 1187, 1130, 1023, 883, 844, 737 cm^{-1}; ^1H NMR (400 MHz) δ = 7.22

(d, J = 12 Hz, 1 H), 7.16 (d, J = 9 Hz, 1 H), 7.01 (dd, J = 9, 9 Hz, 1 H), 6.82 (d, J = 9 Hz, 2 H), 4.07 (t, J = 7 Hz, 2 H), 2.40-2.52 (m, 1 H), 1.79-1.96 (m, 5 H), 1.44-1.52 (m, 2 H), 1.26-1.42 (m, 7 H), 1.16-1.24 (m, 2 H), 0.98-1.12 (m, 2 H), 0.88-0.96 (m, 6 H); MS *m/z* (rel intensity) 436 (M^++1, 2), 435 (M^+, 7), 434 (M^+-1, 5), 433 (1), 352 (19), 351 (61), 350 (47), 349 (15), 252 (52), 251 (100), 250 (34), 237 (9), 195 (6), and 87 (7). Found: *m/z* 435.2819. Calcd for $C_{27}H_{32}D_3F_3O$: M, 435.2825.

3. Synthesis and Characterization of TiO_2 Particles by the *Gel-Sol* Method.

3-1. Preparation of anatase-type TiO_2 particles with anisotropy.

The standard conditions for the preparation of TiO_2 in the present study are as follows. First, a Ti^{4+} stock solution was prepared by mixing TIPO (28.4 g, 0.100 mol) with triethanolamine (TEOA, 29.8 g, 0.200 mol) under dry atmosphere to form a stable complex against hydrolysis of Ti^{4+} a room temperature. After the resulting yellow stock solution consisting of the molar ratio of [TEOA] : [TIPO] = 2 : 1 was kept 1 day at room temperature in a dry air, water was added to make an aqueous stock solution of 0.50 M in Ti^{4+}. Then, the 4.0 or 10 mL of the stock solution in a screw-capped Pyrex bottle was mixed with an aqueous solution of shape controller. The resulting solution was diluted with water, and the pH value of the solution was changed to 10.5 or 11.5 by the addition of an aqueous NaOH or $HClO_4$ solution. After the total volume of the solution was adjusted to 20.0 mL by the further addition of water, the resulting solution was ultrasonicated for 30 min at room temperature. The pH value of the resulting solution was measured and recorded as initial pH (pH_{init}) of the reaction. The concentrations of Ti^{4+} become 0.25 M or 0.10 M. The resulting solution was aged at 100 °C for 24 h for gelation. Finally, the resulting highly viscous gel was placed into a Teflon-lined autoclave and aged at 140 °C for 72 h to nucleate and grow the TiO_2 particles. Obtained particles were collected by centrifugation (18,000 rpm, 30 min) and washed two times with an NaOH (pH 12) aqueous solution, a 2.0 M HNO_3 solution, and water, respectively, by dispersing followed by centrifuging. The resulting particles were dried at 50 °C for 1 day. The details for the preparation were summarized in Table S1.

Table S1. Experimental conditions of TiO_2 synthesis by the *Gel-Sol* method.

TiO_2 particle	Stock solution (mL)	Shape controller	pH_{init}
T1	10	Ethylenediamine (8.0 M, 0.50 mL)	11.38
T2	10	none	10.71
T3	4	Sodium oleate (0.10 M, 4.0 mL)	11.33

3-2. Characterization of anatase-type TiO_2 particles T1-4 by XRD measurements

XRD profiles of TiO_2 particles obtained by the *Gel-Sol* method are shown in Figure S1. All XRD patterns for the particles **T1**-**T4** were in complete agreement with the JCPDS data for anatase-type crystals. For comparison, a XRD profile of a commercial TiO_2 powder of rutile structure is also shown in Figure S1 (e). As readily seen, even a trace of rutile crystals was not observed in **T1**-**T4**. Incidentally, double washing of **T1**-**T4** by 2.0 M HNO_3 with ultrasonic irradiation enabled us to dissolve and remove only $Ti(OH)_4$, if any, in the powders. Then the powders were washed with distilled water, with 0.01 M NaOH, again with distilled water repeatedly to completely purify **T1**-**T4** powders before use.

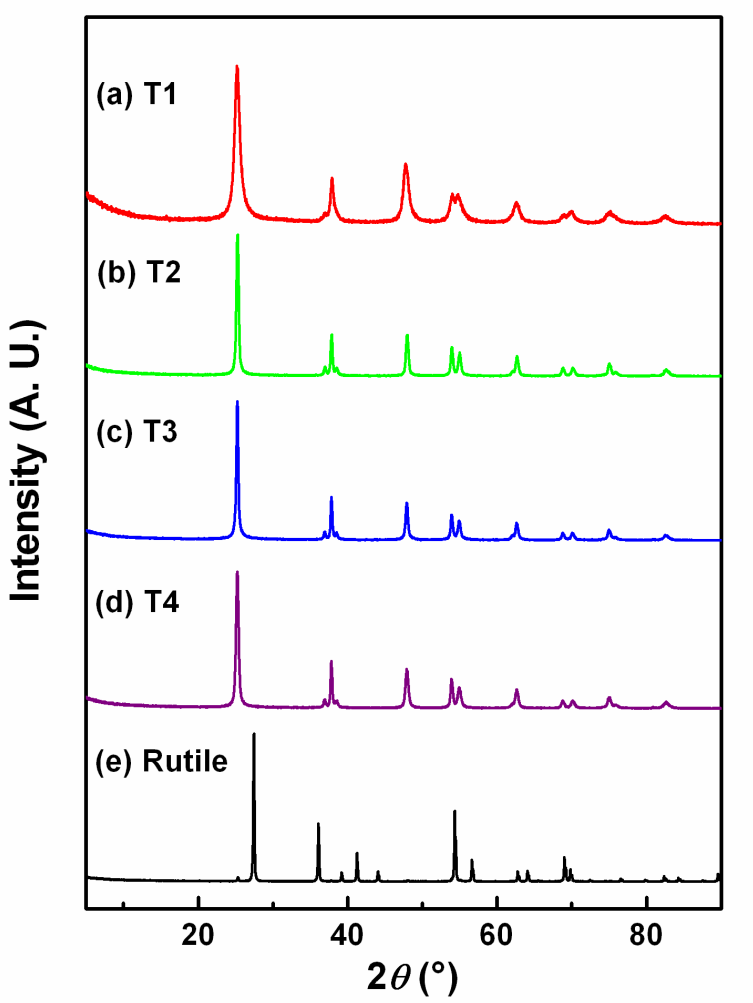


Figure S1. XRD profiles of TiO_2 particles obtained by the *Gel-Sol* method (a) **T1**, (b) **T2**, (c) **T3**, (d) **T4**, and (e) commercial rutile powder with 1-2 μm.

3-3. XPS measurements of T1-T4

The results of XPS on **T1-T4** are shown in Figures S2. The spectra are basically identical with each other, showing the characteristics of pure anatase titania surfaces, expect for a trace of ambient C, N, and B, common to all samples.

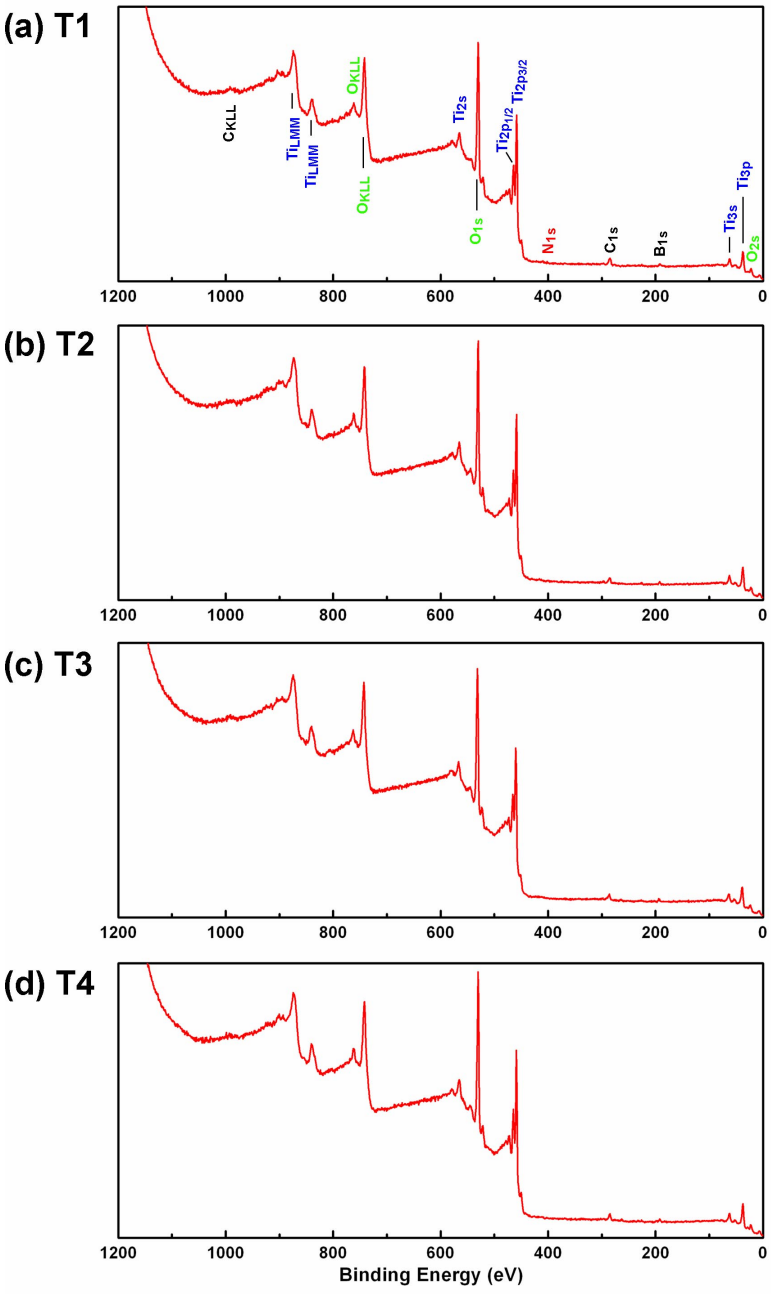
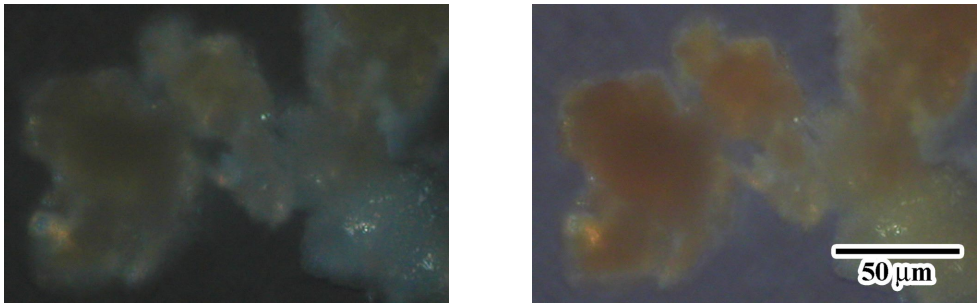


Figure S2. XPS profiles of anatase-type TiO_2 particles prepared by the *Gel-Sol* method (a) **T1**, (b) **T2**, (c) **T3**, (d) **T4** (Mg Kα).

4. POM Observation of the Hybrid LCs.

4-1. Thermal behavior of hybrid L2/T1.

Thermal behavior of equiponderant hybrid of **L2**/**T1** was examined by the POM observation. Compound **L2** formed an N LC phase from 72 to 92 °C. However, the N liquid crystallinity of **L2** was disappeared by the hybridization and none of mesomorphic behavior for **L2**/**T1** was seen. Only decomposition of **L2**/**T1** was observed at *ca.* 240 °C. Polarized optical photomicrographs of **L2**/**T1** at 140 and 240 °C are shown in Figure S3.

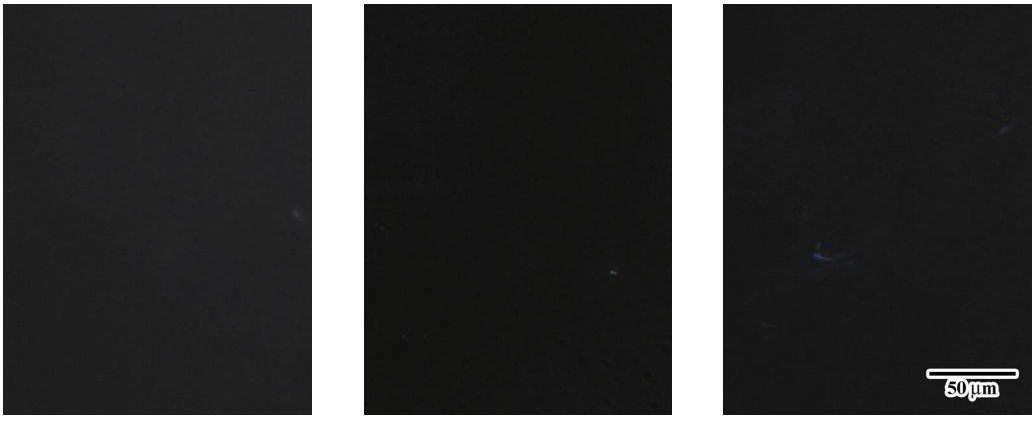


(a) at 140 °C (b) at 240 °C

Figure S3. Polarized optical photomicrographs of **L2**/**T1** on the heating.

4-2. Observation of the thermal behavior of L1/T2, L1/T3, and L1/T4.

To examine the effects of the particle shape and size on the mesomorphic behavior, POM observations of **L1**/**T2**, **L1**/**T3**, and **L1**/**T4** were carried out. Polarized optical photomicrographs of these hybrids at 140 °C were listed in Figure S4 (a)-(c). Birefringence due to the formation of mesomorphic phases was not observed for hybrids **L1**/**T2**, **L1**/**T3**, and **L1**/**T4**. Therefore, anisotropic shape with high aspect ratio such as **T1** is the key for the formation of hybrid LC phase.



(a) **L1**/**T2** at 140 °C (b) **L1**/**T3** at 140 °C (c) **L1**/**T4** at 140 °C

Figure S4. Polarized optical photomicrographs of **L1**/**T2**, **L1**/**T3**, and **L1**/**T4** on the heating.

5. Temperature variable SAXS measurements of the hybrid LCs.

SAXS patterns of hybrid **L1**/**T3** at 70, 90, and 110 °C are shown in Figure S5, representatively. None of peaks due to the periodic interparticle interaction by the formation of liquid crystalline order were observed. Therefore, hybrid **L1**/**T3** exhibited none of mesomorphic behavior.

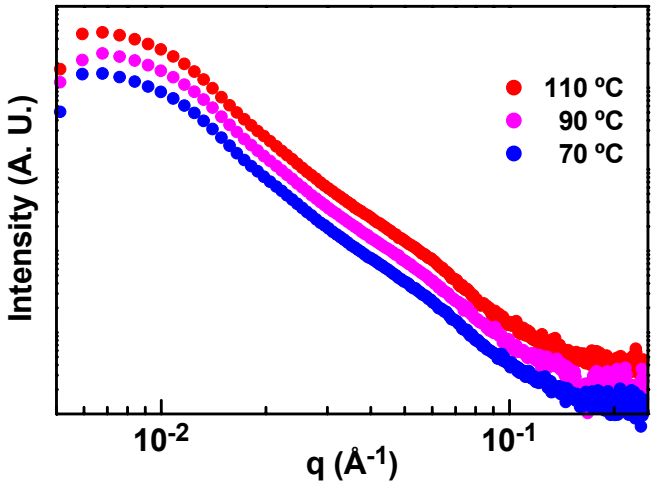


Figure S5. SAXS profiles of hybrid **L1**/**T3** at 70, 90, and 110 °C.