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JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

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Dynamic and Reversible Polymorphism of Self-Assembled Lyotropic Liquid Crystalline Systems Derived from Cyclic Bis(ethynylhelicene) Oligomers

Nozomi Saito,[†,‡] Kiyoshi Kanie,[§] Masaki Matsubara,[§] Atsushi Muramatsu,[§] and Masahiko Yamaguchi*[,‡]

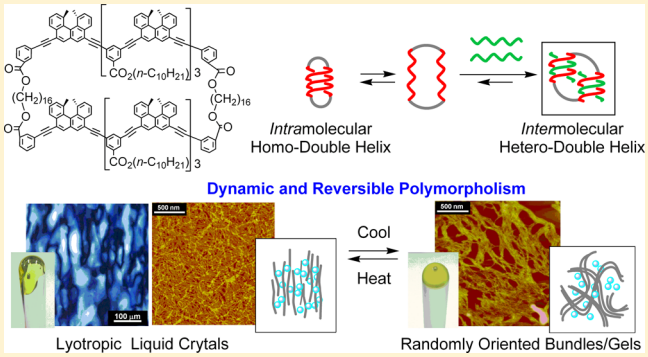
[†]Frontier Research Institute for Interdisciplinary Sciences, Tohoku University , 6-3 Aoba, Sendai 980-8578, Japan

[‡]Department of Organic Chemistry, Graduate School of Pharmaceutical Sciences, Tohoku University, Aoba, Sendai 980-8578, Japan

[§]Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1, Katahira, Aoba-ku, Sendai 980-8577, Japan

Supporting Information

ABSTRACT: A self-assembled lyotropic liquid crystal (LLC) system exhibiting dynamic and reversible polymorphism was developed using the synthetic cyclic ethynylhelicene oligomers cyclobis[(*M*)-D-***n***] (n = 4 and 6), in which two oligomer moieties are connected by two flexible linkers. The cyclic molecular structure was designed to control aggregation properties ranging from the molecular level to the macroscopic level. The cyclic oligomer changed its structure between random coils and an *intra*molecular homo-double helix induced by temperature and solvents. In the presence of pseudoenantiomeric acyclic oligomers, cyclobis[(*M*)-D-**4**] formed trimolecular complexes with a total molecular weight of over 10 000 Da containing two *inter*molecular hetero-double helices. The trimolecular complex formation predominated over bimolecular complex formation. The trimolecular complex self-assembled at high concentrations and formed LLCs composed of anisotropically aligned fibers. The result is in contrast to acyclic systems, which form gels composed of randomly oriented fibers. The LLCs changed into turbid gels composed of randomly oriented bundles upon cooling, and the LLCs were regenerated by heating. This is a notable example of a self-assembled LLC system exhibiting dynamic and reversible polymorphism between two *ordered* structures in a closed system consisting of fully synthetic molecules.



INTRODUCTION

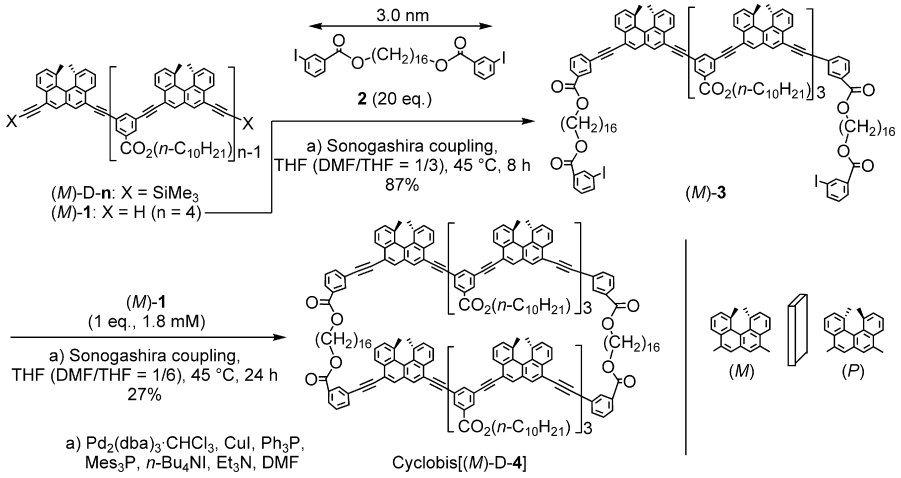
In biological systems, a single protein exhibits dynamic polymorphism at the self-assembly level of nano- to centimeter size, which is switched by environmental factors such as temperature, concentration, ions, ligands, and other chemicals. Dynamic polymorphism is closely related to biological functions, and actin is one of the ubiquitous examples: G-actin is a globular protein with a molecular weight of 42 000 Da, and its molecular shape changes upon complexation with ATP. In the presence of ATP and metal cations, G-actin self-assembles to form polymeric fibers called F-actin, which further self-assemble and form filaments in the presence of binding proteins.[1,2e,g,i] The filaments continue to self-assemble and form nano- to micrometer-scale structures such as lyotropic liquid crystals (LLCs), gels, meshes, and bundles. The dynamic and reversible polymorphism between these structures, which induces repeated changes among ordered structures, is essential in biological functions such as cell division, contraction, and locomotion.[1,2]

The development of such a self-assembled material system, which exhibits dynamic and reversible polymorphism, by a hierarchical bottom-up of small or oligomeric molecules can be a foundation for understanding biological functions and developing stimuli-responsive functional materials. LLCs are attractive for such a material system because of their anisotropic nature, particularly when they exhibit dynamic and reversible polymorphism. In this study, dynamic and reversible polymorphism implies a reversible structural change between two *ordered* self-assembled material systems, in contrast to generally known transitions between ordered LLCs and nonstructured isotropic liquids. A limited number of self-assembled LLC-forming small or oligomeric molecules including synthetic peptides,[3] dyes,[4] and other small molecules[5] exhibit dynamic and reversible polymorphism between two ordered systems in an open system. In such systems, the morphologies are changed by the addition and removal of chemicals, a change in concentrations, and a change of solvents, which require relatively complex manipulations, and repeated switching is not facile. Synthetic self-assembled LLC systems that exhibit dynamic and reversible polymorphism in closed systems induced by external physical energy[6] are more attractive

Received: February 24, 2015
Published: May 5, 2015

DOI: 10.1021/jacs.5b02003
J. Am. Chem. Soc. 2015, 137, 6594−6601

Scheme 1



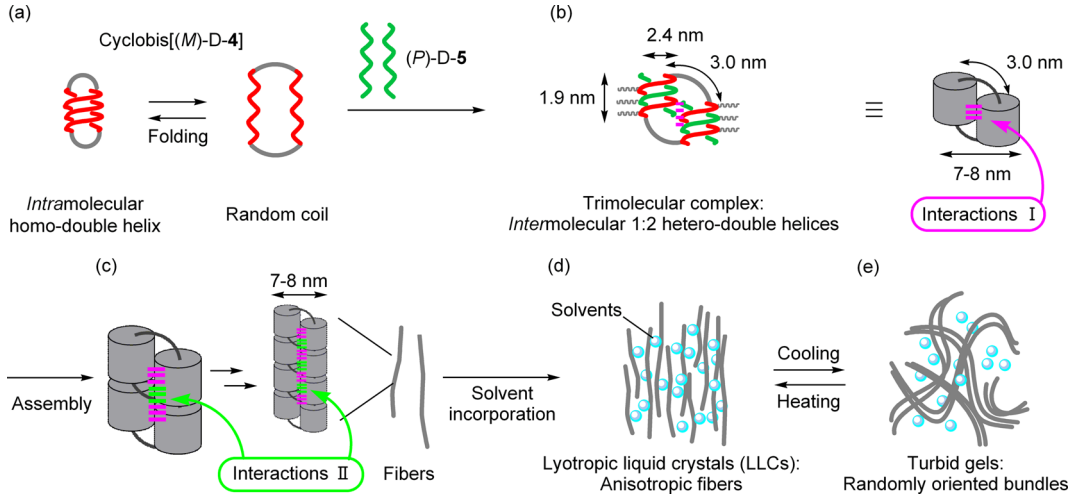


Figure 1. Schematic representation of the molecular-level and self-assembly level structural changes of the cyclobis[(*M*)-D-**4**]/(*P*)-D-**5** system. (a) Formation of an *intra*molecular homo-double helix, (b) formation of a trimolecular complex with *inter*molecular hetero-double helices by interactions I, (c) fiber formation by interactions II between trimolecular complexes, (d) LLC formation involving solvent molecules, and (e) formation of turbid gels composed of randomly oriented bundles upon cooling.

because such systems can exhibit repeated switching with simple manipulations. However, such a system derived from self-assembly of small or oligomeric synthetic molecules, which exhibits a reversible structural change between two *ordered* self-assembled structures, is practically unknown.

Here, we report the formation of self-assembled LLC systems using the synthetic cyclic molecules cyclobis[(*M*)-D-***n***] (Scheme 1), which exhibit dynamic and reversible polymorphism attributed to a temperature change. The cyclic molecular design, as will be discussed below in detail, turned out to be effective in controlling the aggregation properties ranging from molecular level to self-assembly level, which eventually provided an anisotropic self-assembled LLC and exhibited dynamic and reversible polymorphism. At the molecular level, cyclobis[(*M*)-D-***n***] showed a structural change between random coils and an *intra*molecular homo-double helix induced by heat and solvents (Figure 1a). In the presence of enantiomeric acyclic oligomers (*P*)-D-***n***, trimolecular complexes with a total molecular weight of over 10 000 Da containing *inter*molecular hetero-double helices were formed, which predominated over the *intra*molecular homo-double helix (Figure 1b). (1) At the self-assembly level, the trimolecular complex self-assembled and formed LLCs composed of anisotropically aligned fibers at high concentrations (Figure 1c,d). This is in contrast to acyclic systems, for example, (*M*)-D-**4**/(*P*)-D-**5**, which forms gels composed of randomly oriented fibers. This is a notable LLC formed by the self-assembly of synthetic double helix organic molecules.[7,8] (2) The self-assembled system showed dynamic and reversible polymorphism between two *ordered* structures,[9] the LLC and a turbid gel composed of randomly oriented bundles, attributed to a temperature change in a closed system (Figure 1d,e). The results are reminiscent of the self-assembly property and the dynamic and reversible polymorphism of actin, which play important roles in biological systems.

RESULTS AND DISCUSSION

Molecular Design and Synthesis. During our studies on the derivatives of helicene, 1,12-dimethylbenzo[*c*]-phenanthrene,[10] we reported the formation of homo-[11] and hetero-double helices[11d,12] of ethynylhelicene oligomers. By mixing pseudoenantiomers, which are a pair of compounds containing enantiomeric (*P*)- and (*M*)-helicenes with different numbers of helicene units, hetero-double helices were formed.

DOI: 10.1021/jacs.5b02003
J. Am. Chem. Soc. 2015, 137, 6594−6601

The hetero-double helices self-assembled by lateral interactions, named intercomplex interactions, and formed fibers/gels in toluene and vesicles in diethyl ether.[12,13] The properties of the self-assemblies were controllable by changing the side chains and number of helicenes.[12,13] In this study, the cyclic oligomers cyclobis[(*M*)-D-***n***] (*n* = 4 or 6), in which two (*M*)-ethynylhelicene tetramers or hexamers are connected by two flexible hexadecamethylene linkers (Scheme 1), were developed, where "D" represents decyloxycarbonyl side chains, and ***n*** is the number of helicenes contained in one oligomer moiety.

The cyclic structure was designed to form a rigid trimolecular complex containing hetero-double helices, derived from one molecule of cyclobis[(*M*)-D-***n***] and two acyclic pseudoenantiomeric molecules of (*P*)-D-***n***. Two types of intercomplex interactions are conceivable for this trimolecular complex: one is the interactions between two hetero-double helices *in* the trimolecular complexes (Figure 1b, interactions I), and the other is the interactions *between* the trimolecular complex (Figure 1c, interactions II). Interactions I can provide rigidity to the trimolecular complex because of the confined mobility of the hetero-double helices. Interactions II can be driving forces to form self-assemblies. The linker moiety to connect the two hetero-double helices was designed to realize the above concepts. A hexadecamethylene linker of 3.0 nm in length[11c] (Scheme 1) was employed to make the trimolecular complex rigid, because this length is close to the calculated diameter 2.4 nm of a hetero-double helix in which side chains are abbreviated to methoxycarbonyl groups[12b] (Figure 1b). By employing interactions I and II with the cyclic molecular design, aggregation properties ranging from the molecular level to the self-assembly level were successfully controlled, and an anisotropic self-assembled LLC system exhibiting dynamic and reversible polymorphism was developed. The results are described below.

Cyclobis[(*M*)-D-**4**] (*n* = 4) was synthesized in a step-by-step manner (Scheme 1). Sonogashira coupling of desilylated ethynylhelicene (*M*)-**1**[14] and an excess amount of linker **2**[11c] gave (*M*)-**3** in 87% yield. Cyclobis[(*M*)-D-**4**] was obtained by the coupling of (*M*)-**3** and (*M*)-**1** under diluted conditions in 27% yield. Cyclobis[(*M*)-D-**6**] (*n* = 6) was synthesized in a similar manner (Supporting Information Scheme S1).[15]

Formation of Homo-Double Helix. Circular dichroism (CD) and UV–vis studies were conducted for the analysis of random coils and homo-double helix states in solution. Cyclobis[(*M*)-D-**4**] in toluene (2.5×10^{-4} M) was heated at 80 °C, then CD and UV–vis spectra were obtained after reaching a steady state at each temperature. Weak Cotton effects mirror-imaged to those of (*P*)-D-**4** in the random coil state[11a,12a] were obtained at 80 and 60 °C, which indicated cyclobis[(*M*)-D-**4**] in the S-random-coil state, where the equilibrium shifted to the random coil state containing no homo-double helices (Figure 2a and Supporting Information Figure S1). The slight change in CD intensity and a hypochromic shift of UV–vis absorption at 40, 25, and 5 °C indicated a small amount of double-helix formation.

Cyclobis[(*M*)-D-**4**] formed a homo-double helix in trifluoromethylbenzene[16] (5×10^{-4} M) and showed intense CD and a hypochromic shift of UV–vis (Figure 2b), which are different from those of random coils in toluene (Figure 1b and Supporting Information Figure S1). The same spectra (5×10^{-4} M) at 25 and 5 °C indicated the S-homo-double-helix state, where the equilibrium was shifted to the homo-double helix state containing no random coils (Figure 2b). The same

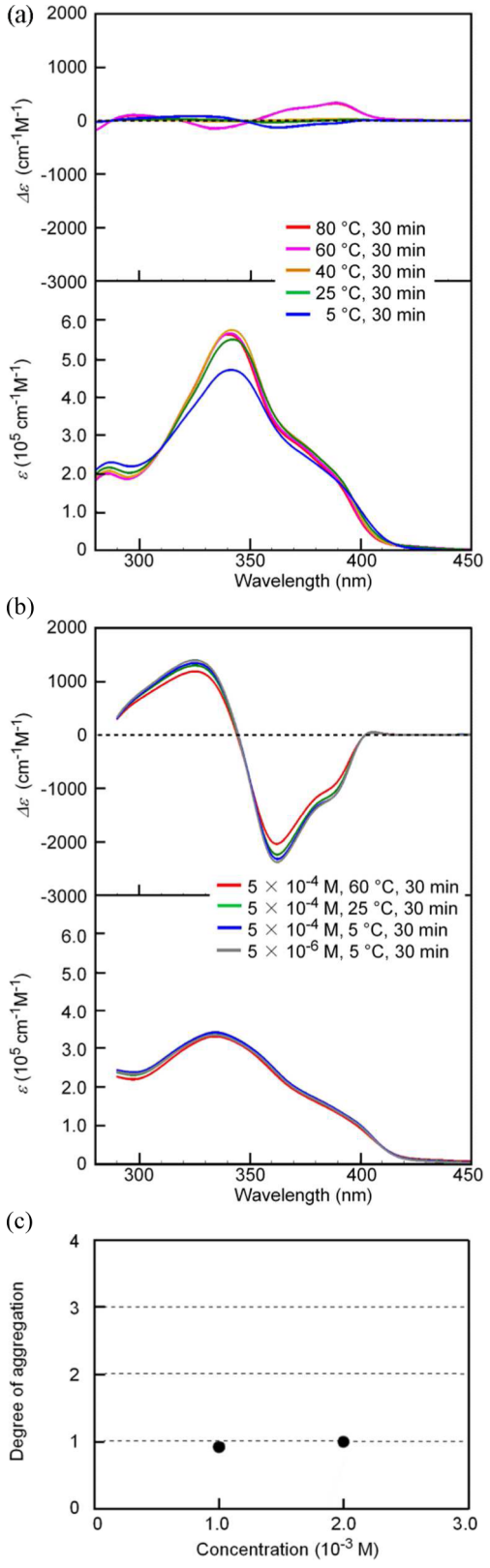


Figure 2. CD (top) and UV–vis (bottom) spectra of cyclobis[(*M*)-D-**4**] in (a) toluene (2.5×10^{-4} M) and (b) trifluoromethylbenzene (5×10^{-4} and 5×10^{-6} M). (c) VPO analysis of cyclobis[(*M*)-D-**4**] (trifluoromethylbenzene, 45 °C).

CD spectrum was obtained at a much lower concentration (5.0×10^{-6} M, 5 °C) (Figure 2b). The molecular weights of the homo-double helix obtained by VPO studies (trifluoromethyl-

DOI: 10.1021/jacs.5b02003
J. Am. Chem. Soc. 2015, 137, 6594–6601

benzene, 45 °C), 4.5×10^3 (1.0×10^{-3} M) and 4.9×10^3 (2.0×10^{-3} M), confirmed the monomeric state of cyclobis[(*M*)-D-**4**] (Figure 2c). The intense CD, the hypochromic shift of UV−vis, their insensitivity to temperature and concentration changes, and the monomeric state determined by VPO studies indicated the formation of an *intra*molecular homo-double helix (Figure 1a) in trifluoromethylbenzene. For comparison, CD spectra of the acyclic oligomer (*M*)-D-**4** (trifluoromethylbenzene, 1.0×10^{-5} M) showed weak Cotton effects typical of the S-random-coil state even at 5 °C (Supporting Information Figure S2). Thus, the *intra*molecular homo-double helix of cyclobis[(*M*)-D-**4**] is thermodynamically more stable than the *inter*molecular homo-double helix of (*M*)-D-**4**.

Cyclobis[(*M*)-D-**6**] also formed an *intra*molecular homo-double helix in trifluoromethylbenzene, as shown by CD and VPO studies (Supporting Information Figure S3a,c). The *intra*molecular homo-double helix of cyclobis[(*M*)-D-**6**] was thermodynamically more stable than that of cyclobis[(*M*)-D-**4**], as suggested by the unfolding of the latter to the S-random-coil state in chlorobenzene by heating at 80 °C (Supporting Information Figure S3b).

Formation of Hetero-Double Helix. The formation of the hetero-double helix was examined using the system of cyclobis[(*M*)-D-**4**] and (*P*)-D-**5** in toluene, which is a weaker helix-forming solvent than trifluoromethylbenzene.[11a,b,e] Previous study showed that the hetero-double helices were thermodynamically more stable than homo-double helices, and that the former formed self-assembly[12] in toluene. Solutions of cyclobis[(*M*)-D-**4**] and (*P*)-D-**5** showed CD spectra (toluene, 2.5×10^{-4} M, 25 °C) of the partial homo-double helix and S-random-coils, respectively (Supporting Information Figures S4 and S5a). When these solutions were mixed in a 1:2 ratio, the experimental CD and UV−vis spectra (toluene, total 2.5×10^{-4} M, 25 °C) were different from the spectra calculated by adding the spectra[15] of cyclobis[(*M*)-D-**4**] and (*P*)-D-**5** in a 1:2 ratio. The steady state was reached after 30 min, showing CD with a positive maximum at 319 nm and a negative maximum at 364 nm, which remained unchanged for 9 h (Figure 3a, top). The $\varepsilon_{365}/\varepsilon_{335}$ value of 0.89 obtained from the UV−vis spectrum was consistent with the formation of the hetero-double helix (Figure 3a, bottom).[12] A Job plot using $\varepsilon_{365}/\varepsilon_{335}$ values showed the composition of the heteroaggregate of cyclobis[(*M*)-D-**4**] and (*P*)-D-**5** to be 1:2 (Figure 3b). The results indicated the formation of the trimolecular complex containing two *inter*molecular hetero-double helices (Figure 1b). When the mixture of cyclobis[(*M*)-D-**4**]/(*P*)-D-**5** was heated to 80 °C, the CD intensity decreased, and the $\varepsilon_{365}/\varepsilon_{335}$ value decreased to 0.77 (Supporting Information Figure S5b), indicating partial disaggregation of the hetero-double helices. It was previously shown that the acyclic (*M*)-D-**5**/(*P*)-D-**4** system completely disaggregated under the same conditions (toluene, total 2.5×10^{-4} M, 80−85 °C).[13a] The hetero-double helices in the trimolecular complex of the cyclobis[(*M*)-D-**4**]/(*P*)-D-**5** system are thermodynamically more stable than the hetero-double helix of (*M*)-D-**5**/(*P*)-D-**4**.

The apparent molecular weights of the heteroaggregate was determined by VPO studies (60 °C) using the cyclobis[(*M*)-D-**4**]/(*P*)-DF-**6** system in fluorobenzene[15] because of the higher solubility of this system in the solvent than the cyclobis[(*M*)-D-**4**]/(*P*)-D-**5** system: 1.3×10^4 at total 1.0×10^{-3} M and 1.2×10^4 at total 2.0×10^{-3} M. The result coincided with the calculated molecular weight of 12 370 of a trimolecular complex of cyclobis[(*M*)-D-**4**]/(*P*)-DF-**6** (Figure 4). It was confirmed

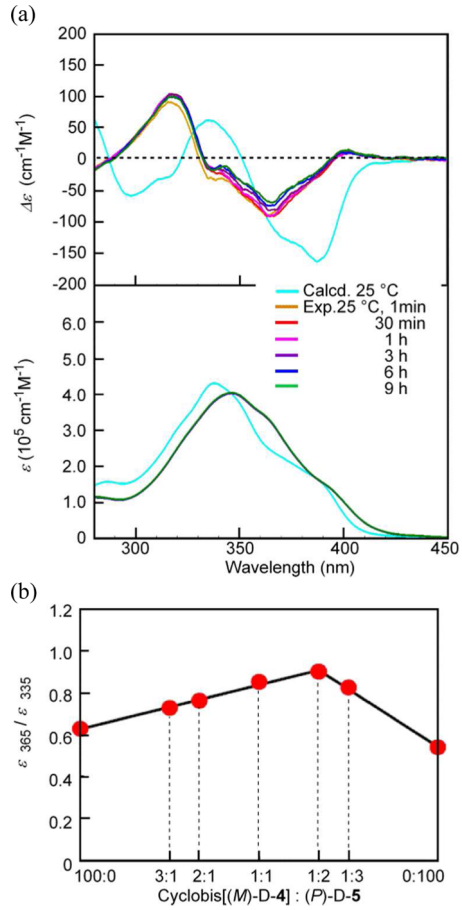


Figure 3. (a) CD (top) and UV−vis (bottom) spectra of a 1:2 mixture of cyclobis[(*M*)-D-**4**]/(*P*)-D-**5** (toluene, total 2.5×10^{-4} M, 25 °C). The spectra were obtained at the indicated times after mixing. The calculated spectra obtained by adding the spectra of cyclobis[(*M*)-D-**4**] and (*P*)-D-**5** (toluene, 2.5×10^{-4} M, 25 °C) are also shown (Supporting Information Figure S5a). (b) Job plot of $\varepsilon_{365}/\varepsilon_{335}$ (toluene, total 2.5×10^{-4} M, 25 °C, 24 h) against ratio of cyclobis[(*M*)-D-**4**] to (*P*)-D-**5**. Approximated straight lines are also shown.

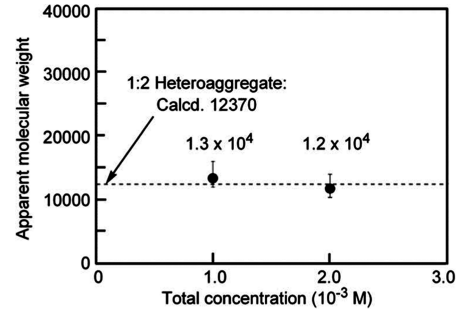


Figure 4. Apparent molecular weights of the complex in 1:2 mixture of cyclobis[(*M*)-D-**4**]/(*P*)-DF-**6** (fluorobenzene, 60 °C). The measurements were conducted between 30 min and 1 h after mixing. The circle and vertical lines represent the average and the range of five obtained results, respectively. The dashed lines show the calculated molecular weight (12 370) of the trimolecular complex.

that the cyclobis[(*M*)-D-**4**]/(*P*)-DF-**6** system (fluorobenzene, total 2.5×10^{-4} M, 60 °C, 24 h) showed CD and UV−vis spectra (Supporting Information Figure S6a) similar to those of the cyclobis[(*M*)-D-**4**]/(*P*)-D-**5** system (Figure 3a). The Job

DOI: 10.1021/jacs.5b02003
J. Am. Chem. Soc. 2015, 137, 6594−6601

plot indicated 1:2 stoichiometry (Supporting Information Figure S6b). On the basis of these results, it was concluded that trimolecular complexes containing hetero-double helices (Figure 1b) were formed in both cyclobis[(*M*)-D-**4**]/(*P*)-DF-**6** and cyclobis[(*M*)-D-**4**]/(*P*)-D-**5** systems.

Note that the trimolecular complex containing *inter*molecular hetero-double helices predominated over the *intra*molecular homo-double helix (Figure 1b). The formation of the stable trimolecular complex can be due to the lateral tight packing of two hetero-double helices by interactions I (Figure 1b). It was also noted that a 1:1 bimolecular complex was not observed, which indicated high thermodynamic stability of the 1:2 trimolecular complex.

Formation of LLCs. When the total concentration of cyclobis[(*M*)-D-**4**] and (*P*)-D-**5** was increased in toluene, an LLC was formed. Solutions of cyclobis[(*M*)-D-**4**] and (*P*)-D-**5** at 1.0×10^{-2} M were mixed in a 1:2 ratio, heated at 100 °C for 30 min, and then allowed to stand at ambient temperature for 5 days. The mixture gradually changed into a viscous fluid (Figure 5a). Polarized optical microscopy (POM) showed

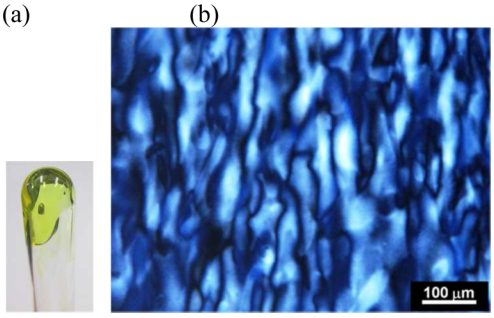


Figure 5. (a) Visual image of the LLC (toluene, total 1.0×10^{-2} M) in a glass tube of 13 mm diameter at 25 °C, in which an aluminum ball of 2 mm diameter is placed. (b) POM image of a 1:2 mixture of cyclobis[(*M*)-D-**4**]/(*P*)-D-**5** (toluene, total 1.0×10^{-2} M, rt, 5 days) observed at 25 °C.

birefringence with a polydomain texture typical of the nematic LLC phase (Figure 5b). Viscous LLCs were also obtained in other aromatic solvents such as benzene, ethylbenzene, and *o*-, *m*-, and *p*-xylene under the same conditions (total 1.0×10^{-2} M), and the POM images were similar to those observed in toluene (Supporting Information Figure S7). The small-angle X-ray scattering (SAXS) profile of the LLC in toluene showed an ellipsoidal diffraction pattern with a broad center at around 9 nm, which was perpendicular to the nematic director observed by POM using an identical sample (Supporting Information Figure S8).[17] The results indicated regular periodicity with a distance of ca. 9 nm perpendicular to the nematic director, which was ascribed to the width of mesogens with surrounding solvents. Atomic force microscopy (AFM) studies of the LLC showed partially aligned fibers (Figure 6) of 7−8 nm diameter (Supporting Information Figure S9), which was consistent with the result of the SAXS analysis. The diameter is slightly larger than the diameter (4.8 nm) of the trimolecular complex, estimated by doubling the calculated diameter (2.4 nm) of a hetero-double helix with methoxycarbonyl side chains,[12b] probably because the alkyl moiety of decyloxycarbonyl side chains (Supporting Information Figure S10) is included (Figure 1b).

A plausible mechanism of the LLC formation in the cyclobis[(*M*)-D-**4**]/(*P*)-D-**5** system is provided as follows. Cyclobis[(*M*)-D-**4**] and (*P*)-D-**5** first aggregate in a 1:2 ratio and form the trimolecular complex by interactions I (Figure 1b). Two hetero-double helices in the trimolecular complex are slightly offset along the helical axis, which exert interactions II, and the trimolecular complexes form the fibers of 7−8 nm diameter (Figure 1c). The fibers are anisotropically aligned and formed nematic LLC involving the solvent molecules (Figure 1d).

LLC formation of the cyclobis[(*M*)-D-**4**]/(*P*)-D-**5** system in aromatic solvents is significantly different from the gelation of the (*M*)-D-**4**/(*P*)-D-**5** system containing acyclic oligomers. Although both systems form fibers, their alignments are different. In the cyclobis[(*M*)-D-**4**]/(*P*)-D-**5** system, the fibers are anisotropically aligned, and the solvents are contained among the fibers, maintaining their fluidity. On the other hand, the fibers are randomly oriented in the (*M*)-D-**4**/(*P*)-D-**5** system, as indicated by the POM image without birefringence, and the solvent is immobilized in the network. Interactions I and II, derived from the cyclic ethynylhelicene oligomers with the linkers, effectively provided the anisotropy to the fibers. It is indicated that judicious molecular design can be used to control the morphology of self-assembly and the alignment of the resulting fibers. It should also be noted that the LLC formation by self-assembly of synthetic double-helix-forming molecules[11−13,18,19] has not been previously reported,[7] and the results are reminiscent of the property of biological double-helical molecules and polymers[8] such as DNA and RNA,[20]

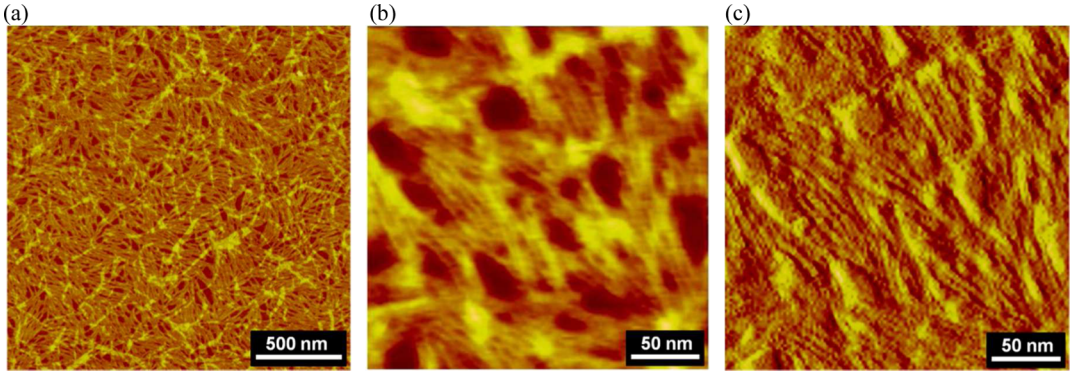


Figure 6. AFM (a and b) height and amplitude images (c) of a 1:2 mixture of cyclobis[(*M*)-D-**4**]/(*P*)-D-**5** (toluene, total 1.0×10^{-2} M, rt, 5 days). The AFM samples were prepared by diluting the LLC (toluene, total 1.0×10^{-2} M, rt, 5 days) to ca. 1×10^{-4} M, followed by drying on a mica surface under ambient conditions.

DOI: 10.1021/jacs.5b02003
J. Am. Chem. Soc. 2015, 137, 6594−6601

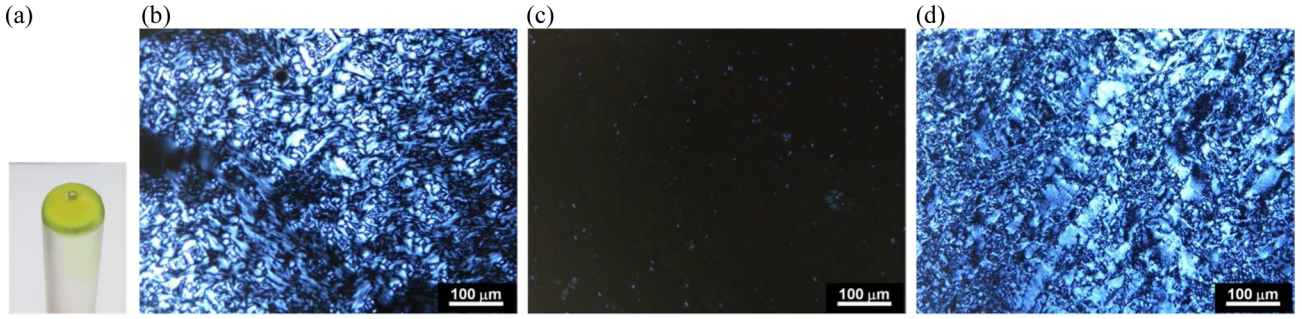


Figure 7. (a) Visual image of the turbid gel obtained upon cooling the LLC (toluene, total 1.0×10^{-2} M, rt, 5 days) in a glass tube of 13 mm diameter at −60 °C for 30 min, in which an aluminum ball of 2 mm diameter is placed. POM images of a 1:2 mixture of cyclobis[(*M*)-D-**4**]/(*P*)-D-**5** (toluene, total 1.0×10^{-2} M, rt, 5 days) observed at (b) 25 °C, (c) −60 °C, and (d) 25 °C after cooled at −60 °C are also shown. The mixture was cooled or heated at the rate of 2 °C min^{-1}.

polysaccharides,[21] and actin[2,22] that form LLCs in aqueous media.

Formation of Randomly Oriented Bundles and Gels: Dynamic and Reversible Polymorphism. The LLC of cyclobis[(*M*)-D-**4**]/(*P*)-D-**5** exhibited dynamic and reversible polymorphism attributed to a temperature change in a closed system. When the nematic LLC phase in toluene was heated to 100 °C, the visual and POM images did not change (Supporting Information Figure S11). This shows the high thermal stability of the aligned fibers. On the other hand, when the LLC was cooled, its transparency decreased and its viscosity increased as observed with the naked eye. The LLC changed into a turbid gel at −60 °C, which did not show a gravitational flow when the glass tube was turned upside down (Figure 7a). POM observation was conducted by cooling or heating the LLC at a rate of 2 °C min^{-1}. The birefringence observed at 25 °C started to turn darker at −20 °C and almost disappeared at −60 °C (Supporting Information Figure S12). These temperature-dependent changes were reversible, and the birefringence was recovered when the mixture was warmed to 25 °C (Figure 7b–d and Supporting Information Figure S12). Similar results were obtained when the cooling/heating cycle was repeated (Supporting Information Figure S13), and when the mixture was cooled or heated at a rate of 10 °C min^{-1} (Supporting Information Figure S14). The thermal event was characterized by differential scanning calorimetry (DSC). DSC thermograms showed broad endothermic and exothermic events between −10 and −60 °C (Supporting Information Figure S15) in the heating and cooling processes, respectively, which are consistent with the POM observation.

For the structural analysis, the mixture cooled at −60 °C was rapidly diluted with toluene at the same temperature, and a portion of which was immediately dropped onto a freshly cleaved mica surface, then the solvent was removed under reduced pressure.[15] AFM analysis indicated the formation of an entangled network composed of thick bundles of mostly 40–300 nm width (Figure 8 and Supporting Information Figure S16). The results showed that the thin fibers of 7–8 nm width in the LLC self-assembled to form thick bundles upon cooling, which provided a randomly oriented and entangled three-dimensional network of the bundles. It is presumed that cooling promoted the aggregation of thin fibers expelling solvents, which resulted in the bundle formation. As a result, the anisotropy of the cyclobis[(*M*)-D-**4**]/(*P*)-D-**5** system in the LLC state was lost, and the system changed into the turbid gel (Figure 1e).

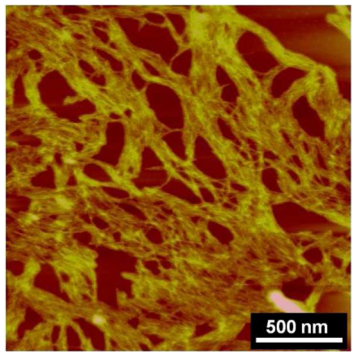


Figure 8. AFM height image of a 1:2 mixture of cyclobis[(*M*)-D-**4**]/(*P*)-D-**5** (toluene, total 1.0×10^{-2} M, rt, 5 days). The AFM samples were prepared by cooling the LLC (toluene, total 1.0×10^{-2} M, rt, 5 days) at −60 °C for 30 min, diluting to ca. 1×10^{-4} M at −60 °C, and then drying in vacuo on a mica surface with the temperature increase from −60 to 25 °C.

The cyclobis[(*M*)-D-**4**]/(*P*)-D-**5** system composed of fully synthetic molecules showed dynamic and reversible polymorphism between the LLC composed of anisotropically aligned fibers and the turbid gel composed of randomly oriented bundles, which is reminiscent of the polymorphism of actin, which plays important roles in biological functions. Such dynamic and reversible polymorphism of self-assembled LLC systems caused by physical stimuli, such as a temperature change, in a closed system has rarely been observed. It is also worth noting that this is a switching between two *ordered* structures,[9] in contrast to the generally known transitions between an LLC and nonstructured isotropic liquids.[23] The use of large-molecular-weight trimolecular complexes of over 10 000 Da is another protein-like notable feature of this system.

■ CONCLUSIONS

A self-assembled LLC system, which exhibits dynamic and reversible polymorphism, was developed using synthetic cyclic ethynylhelicene oligomers. The cyclic oligomers changed their structure between random coils and an *intra*molecular homo-double helix induced by temperature and solvents. By adding pseudoenantiomeric acyclic oligomers, trimolecular complexes with a total molecular weight of over 10 000 Da containing two *intra*molecular hetero-double helices were formed. The trimolecular complex continued to self-assemble at high concentrations and formed LLCs composed of anisotropically aligned fibers. This is a notable LLC formed by the self-

DOI: 10.1021/jacs.5b02003
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assembly of synthetic double helix organic molecules. The LLCs changed into turbid gels composed of randomly oriented bundles upon cooling and were regenerated by heating; the interconversion was reversible. The cyclic molecular design controlled the properties from the molecular level to the self-assembly level, which provided a notable self-assembled synthetic LLC system exhibiting dynamic and reversible polymorphism between two *ordered* structures in a closed system. The results are reminiscent of the self-assembly property and the dynamic and reversible polymorphism of actin, which plays important roles in biological functions. Such materials should have potential applications as stimuli-responsive dynamic functional materials.

■ ASSOCIATED CONTENT

Supporting Information

Full experimental details including general methods, synthesis, analysis, additional figures, and ^{1}H and ^{13}C NMR spectra. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b02003.

■ AUTHOR INFORMATION

Corresponding Author

*yama@m.tohoku.ac.jp

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by Grants-in-Aid for Scientific Research (No. 21229001 to M.Y.) from the Japan Society for the Promotion of Science (JSPS), Grant-in-Aid for Scientific Research for Young Scientists (B) (No. 25860003 to N.S.) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan, and Uehara foundation. N.S. also acknowledges Tohoku University Frontier Research Institute for Interdisciplinary Sciences (FRIS) for their financial support.

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