

Contribution

Control of Superstructures of Liquid-Crystalline Molecules Using Lateral Intermolecular Interactions

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1. Introduction

In May 1997, I was thinking “Should I change my chemistry?” I had been doing projects in organic chemistry from my student days, and at that time I was a 35 years old-assistant professor. I could not stop thinking about that idea. Then, to expand the scale of my chemistry, I was thinking that I have to start a chemistry which was different from what I was studying. Then, I decided to go the USA or Europe to learn supramolecular chemistry and materials science. However, at that time I had no connection with professors in the USA or Europe. So I sent mails to professors who were doing nice work in those chemistry fields, to ask for a postdoctoral position. The first person who gave me the offer for the position was Professor Timothy M. Swager at Massachusetts Institute of Technology

(MIT). He is an authority in the field of supramolecular chemistry and materials science. Fortunately, his reply said “when could you come here?” And I started my study at MIT. On the first day, Prof. Swager gave me a sheet of paper on which a simple figure was written (Figure 1). There was an arrow at the center of a bent rod in the lateral direction. And he said “if you synthesize these kinds of molecules, interesting phenomena are observed.” It seemed to be a study on “liquid crystals”. Later, I checked the words “liquid crystal” with my English-Japanese dictionary, and realized that “liquid crystal” is a state between crystal and liquid. However, I could not understand the value of the new project at that time. “What is liquid crystal?” This simple question remained in my mind after knowing the meaning of the word. It was the start from zero (no knowledge about liquid crystals).

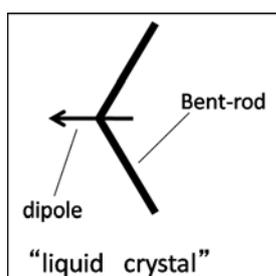


Figure 1. Design of a liquid crystalline molecule which I had seen at the first time.

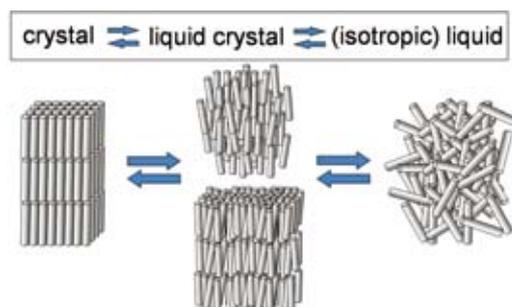


Figure 2. Molecules in crystal, liquid crystal, and (isotropic) liquid states.

As shown in Figure 2, a liquid crystal is an intermediate state between crystal and (isotropic) liquid. It has fluidity with directional and positional orders. Rod- and disk-like molecules tend to have liquid crystallinity. For examples (Figure 3), in the liquid crystal phases of rod-like molecules, nematic, smectic A, and smectic C phases are known. In those of disk-like molecules, nematic and columnar phases are known. Additionally, cubic phases which are three-dimensional and optically isotropic are known.

Most of liquid crystalline molecules used in liquid crystal displays have a rod shape like an "I" (Figure 4 left). The I-shaped molecules are spinning rapidly around the molecular long axes in liquid crystal phases, and this spin movement is important to stabilize the liquid crystal phase because the spinning suppresses crystallization of the molecules at the lower temperature in the liquid crystal range. However, bent rod molecules (V-shaped molecules) (Figure 4 right) cannot spin smoothly around their molecular long axes, which leads to

destabilization of the liquid crystal phase.

I-shaped liquid crystalline molecules possessing a polar substituent at the molecular terminal are known and those molecules respond to an electric field. For example, 4-cyano-4'-pentylbiphenyl (5CB) is used for liquid crystal displays and the molecule changes its orientation by applying a voltage. As shown in Figure 5 (the molecular dipoles are indicated an arrow), by applying an electric field, the molecules align in parallel. The polarity in the direction of the molecular long axis does not suppress the molecular spinning but organizes the rod-like molecules one-directionally.

However, in I-shaped molecules possessing a lateral molecular polarity, their spinning is suppressed by intermolecular dipole-dipole interactions leading to destabilization of the liquid crystal phase. In particular, a molecule possessing a lateral dipole at its center cannot spin smoothly, which easily causes recrystallization.

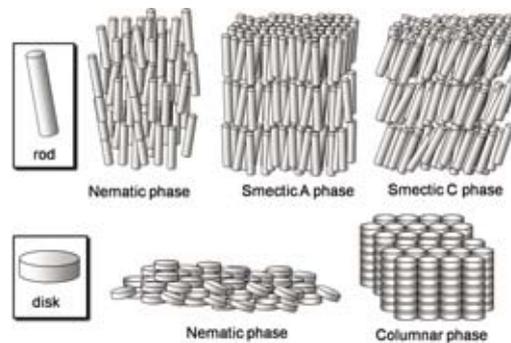


Figure 3. Liquid crystal phases of rod- and disc-like molecules.

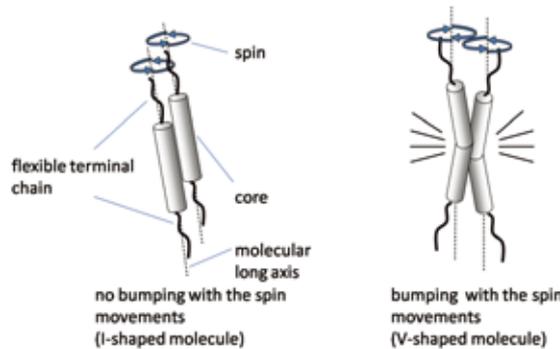


Figure 4. Difference in the behaviors of I- and V-shaped liquid crystalline molecules.

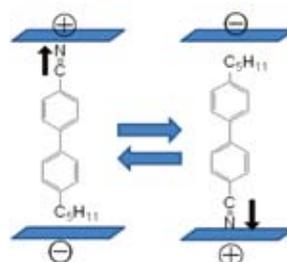


Figure 5. Movement of 5CB molecule under applying a voltage.

Now, I know that the molecular design given by Prof. Swager had two disadvantages (V-shape and a central lateral dipole) for generation of stable liquid crystal phases. The molecular designs are not suitable for preparation of liquid crystalline molecules exhibiting stable liquid crystal phases. That was a very challenging project. During the first three months in MIT, I synthesized 30 kinds of molecules with a bent rod shape and a central lateral dipole. As a matter of course, those molecules did not show any liquid crystallinity and they crystallized easily.

However, after a lot of trial and error, I found a hint to generate a stable liquid crystal phase possessing a V-shape and a lateral central dipole. Separation of anchoring parts and spinning parts was necessary to generate a stable liquid crystal phase.¹ The bent rod part and the central lateral dipole work as an anchor to stop the molecular movement. But if there are spinning parts in the molecule, the parts keep spinning and it suppresses the crystallization of the molecules thus stabilizing the liquid crystal phase.¹ And these spinning parts should be separated from the anchoring part to have a higher effect in stabilization of liquid crystal phases.

This concept can be expanded to synthesis of other liquid crystalline molecules possessing strong intermolecular interactions. If some parts of the molecules keep spin, vibration, and slide movements, the molecules do not crystallize and maintain their liquid crystal phases. Though this concept might not be a new one, I learned this in the one year study at MIT.

After that, as my project, I have been selecting synthesis of novel liquid crystalline molecules which have a large lateral interaction. The concept is based on “keep on moving parts of the molecule”.

2. Introduction of Dipole-Dipole Interaction in the Lateral Direction at the Molecular Center

Compounds **1** and **2** were synthesized in the project at MIT (Figure 6).² These molecules have a thiophene ring with two cyano groups at their center and have a large dipole moment (more than 6 debye as the calculated values). Compound **1** with shorter molecular length gives an unstable liquid crystal phase in which a nematic phase is observed as a super cooled state at 26 °C below the melting point only on cooling. The phase transition from the liquid crystal to the crystal phase proceeded instantaneously. Spinning of the molecules is suppressed strongly because they have a bent rod shape and a large molecular dipole in the direction of the short molecular axes. However, to my surprise, compound **2** which introduced one benzene ring into both core-terminals of **1** exhibited very stable liquid crystal phases. Temperature ranges of its nematic and smectic A phases are 160-252 and 135-160 °C, respectively. This improvement in the stabilization of the liquid crystal phases originated mainly by introduction of the spinning parts into the molecule. An increase of the aspect ratio (= molecular length / molecular width) and an increase of intermolecular interactions by introduction of the two benzene rings and two ester moieties are also thought to be the reasons for the stabilization.

Compound **3** (Figure 7a) was the first liquid crystalline compound synthesized in Chiba university after the end of the MIT project.³ It has a highly bent rod shape, and a large dipole moment. Two rod-like mesogenic cores were linked with -CO-NR-CO- (R = alkyl chain) to synthesize a U-shaped molecule which had a 12 debye molecular dipole. This compound showed a stable smectic A phase at 98-199 °C (Figure 7b). In the XRD of **3**, two layer distances were observed (Figure 7c). In general, smectic A phases have only one layer distance. After heating and cooling cycles, these two layer distances converged into one layer distance. This molecule has a strong molecular dipole, and the dipole-dipole interaction between the molecules are very strong. The neighboring molecules in the layer cannot

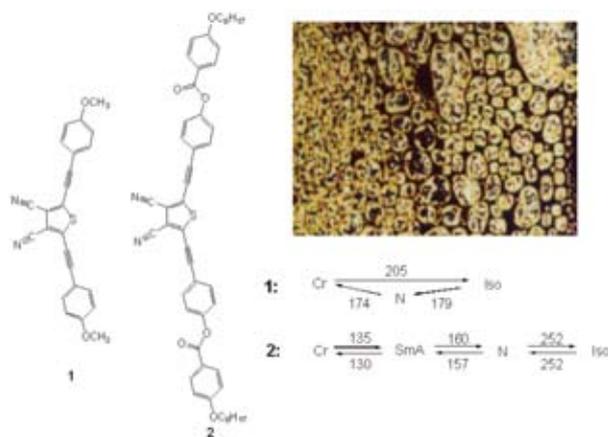


Figure 6. Molecular structures of **1** and **2**, their phase behaviors (Cr: crystal, N: nematic phase, Iso: isotropic liquid, SmA: smectic A phase) and polarized light microphotograph of **2** in the nematic phase.

slide smoothly in the direction of their molecular long axes because of the strong intermolecular interaction. Further, as shown in Figure 7d, each molecule has two mesogenic cores possessing a terminal chain, but it has only one terminal chain at the linkage side. The volume balances of the alkyl chains are different between one end and the other end of the molecule. So it is assumed that the two types of layer structures are generated by this unbalance. One has no interdigitation between the adjacent layers and the other has interdigitation between the layers. The difference between the two layer distances agreed with the length of the alkyl chain interdigitated.

Then, a more simple molecule (4) with a large dipole and

a bent-rod shape was designed and synthesized (Figure 8a). It exhibited a columnar liquid crystal phase (Figure 8b).⁴ In compound 4 there are three alkoxy groups which can donate electrons to the benzene ring and the carbonyl groups to prevent water molecules from attacking at the carbonyl-carbon atoms. So, compound 4 is a stable acid anhydride, and can be purified by column chromatography and recrystallization. Based upon the X-ray structure of 3,4,5-trimethoxybenzoic acid anhydride (Figure 8c) and the molecular model, the strong dipole-dipole interactions between the molecules organizes them into a columnar molecular aggregate in an uneven parallel manner (Figure 8d).

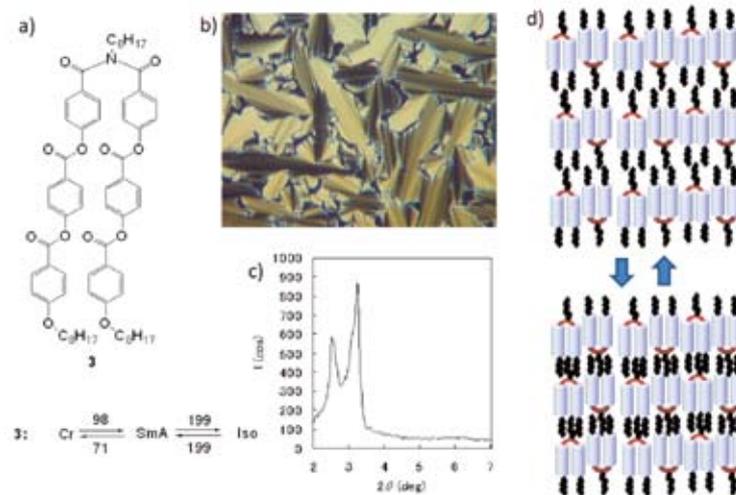


Figure 7. a) Molecular structure of 3 and its phase behavior (Cr: crystal, SmA: smectic A phase, Iso: isotropic liquid), b) polarized light microphotograph of 3 in the smectic A phase, and c) XRD chart of 3, d) molecular packing models indicating two layer distances.

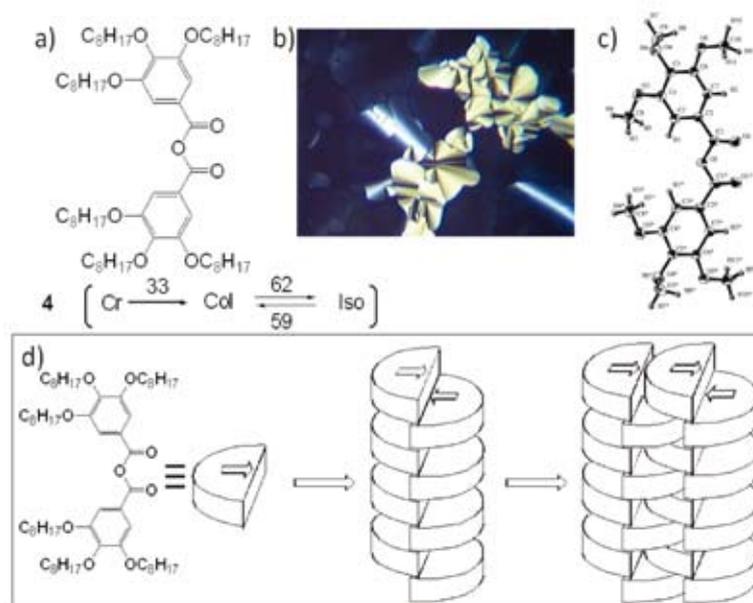


Figure 8. a) Molecular structure of 4 and its phase behavior (Cr: crystal, Col: columnar phase, Iso: isotropic liquid), b) polarized light microphotograph of 4 in the columnar phase, c) X-ray structure of 3,4,5-trimethoxybenzoic acid anhydride, and d) molecular packing models indicating of 4.

induction, though the molecule has no chirality. Spontaneous chiral induction is often observed in crystal phases, but in general, the phenomenon is not observed in fluids such as liquids or liquid crystals. It was assumed that the phenomena took place by a network constructed with rigid intermolecular hydrogen-bonds. From our previous results, it is also thought that the spontaneous chiral induction originates in twisted conformations of the ester moiety.⁸ Though the molecule does not have any chirality, an ester moiety (-CO-O-) has a left-handed or right-handed twist at the C-O single bond between the C=O and O. At the first stage, the molecules with left-handed and right-handed twists are generated in the ratio of 1:1, and then the molecules with the same chirality are organized into a molecular aggregate. These induced chiralities are fixed in each of the domains.

Furthermore, I planned to introduce a strong hydrogen bonding site, a urea moiety, into a molecule (Figure 11a).⁹ The urea molecules are self-assembled into a linear molecular aggregate as shown in Figure 11b. Compounds **7a-c** have six bulky alkyl chains at the terminal ends of their molecules, and the intermolecular steric repulsion generates a torsion angle

between the -NH-CO-NH- faces of the adjacent molecules in their column to lead a helical columnar superstructure. Only the central part of the column has the polar urea moieties and the peripheral part of the column has non-polar alkyl chains. Usually, neighboring polar columns have an anti-parallel arrangement to cancel out their polarity and those highly stabilized columns cannot change the direction of the polarities in the liquid crystal phase. However, in the structures of **7a-c**, the inter-columnar dipole-dipole interaction is much smaller than those of other columnar liquid crystalline compounds because of the long inter-columnar distance between the polar sites. In addition, the repeat distance of the central linear urea moieties is 4.7 Å, and their benzene rings cannot have a strong intermolecular interaction because the distance 4.7 Å between the benzene rings is too long. This structure resembles an old seismically isolated structure of the five-storied pagoda of Horyuji Temple (Figure 11c), which is the oldest wooden building in the world. All the stories are supported by only one big and long log pillar which goes through the center of the pagoda. When an earthquake happens, the pagoda does not collapse because of the suppleness of the wooden pillar. Our

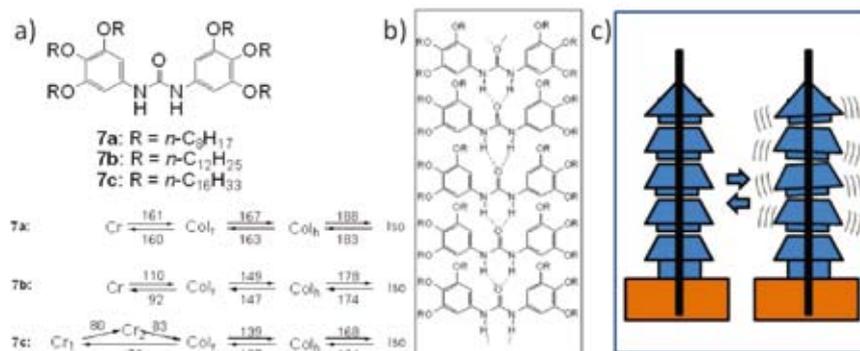


Figure 11. a) Molecular structure of **7a-c** and their phase behavior (Cr: crystal, Col_r: rectangular columnar phase, Col_h: hexagonal columnar phase, Iso: isotropic liquid), b) columnar aggregate of the urea molecules (the hydrogen-bonds are indicated by the dotted lines), and c) an old seismically isolated structure of the five-storied pagoda of Horyuji Temple.

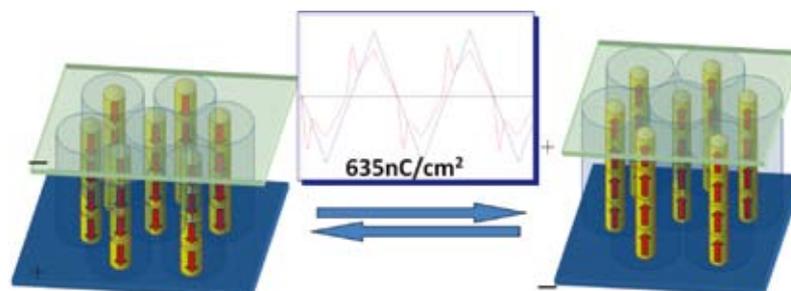


Figure 12. Polar switching of the columns of **7c** by applying a triangular wave voltage. The chart indicates the voltage (blue line) and current (red line). On the current line, switching current peaks were observed repeatedly.

urea molecules also have a strong linear hydrogen bond network at the center of the column, while other parts of the molecules do not have strong interactions with the neighboring molecules so the columns are supple and each urea molecule is swaying. Accordingly, the polar molecules in the flexible polar column cooperatively change their dipoles from one direction to the other, so the polarity of the columns can change directions (Figure 12). The chart shows the change in the current while applying a triangular wave voltage to compound **7c** in the cell capacitor in the columnar liquid crystal phase. The directional change of each molecule originates in the conformational change of the urea moiety. So far, there have been a few reports of polar switching of chiral molecules in columnar phases,¹⁰ but there is no example of polar switching of achiral molecules in columnar phases.¹¹ After report of our study about this switching behavior, some scientist claimed that the switching peaks comes from movement of some ionic impurities. Later, the polar switching of columns was proved by the detailed experiments of the second harmonic generation.¹² Now, stabilization of the polar states is tried by increasing the inter-columnar distance or increasing the energy gap in the switching. In near future, we would like control the polar directions column by column to realize high density memory devices.

4. Introduction of Lateral Perfluoroarene-Arene Interaction

In 1960, Patrick and Prossor found that hexafluorobenzene (mp 5.0 °C) and benzene (mp 5.4 °C) gave a 1:1 complex which crystallized (mp 23.7 °C) at room temperature, and the history of perfluoroarene-arene interactions started after this discovery.¹³ This force is composed of van der Waals and electrostatic interactions, and the energy is 3.7-5.6 kcal/mol¹⁴ which is almost the same level as that of one hydrogen bond. To the best of our knowledge, only two examples are known for stabilization of liquid crystal phases by perfluoroarene-arene interaction.¹⁵ In our laboratory, the simple compound **8** possessing one perfluorophenyl and one trialkoxyphenyl group was synthesized (Figure 13a).¹⁶

As we expected, the molecules generated strong perfluoroarene-arene interaction between the different kinds of π -faces to exhibit a columnar phase. Because of the bent-rod shape of the molecule **8'** (Figure 13b) calculated as that in vacuum, generation of a macroscopic polarity of the column was expected. However, the switching behavior was not observed under application of a triangular wave voltage, which might be suppressed by the strong perfluoroarene-arene interaction between the molecules. Probably, a column structure in which each molecule interacts with the neighboring molecules only with its central part (as shown in the columnar structure of **7**) is necessary for realization of polar switching. In POM, tape-like textures were observed, which indicated the strong intermolecular interaction (Figure 14a). From the two-dimensional XRD (Figure 14b), it was confirmed that disks are composed with two molecules stacked in the column.

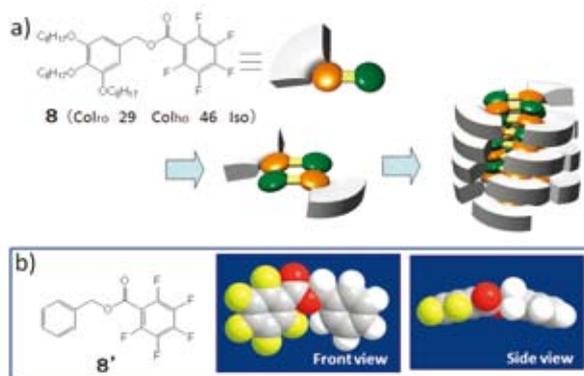


Figure 13. a) Schematic representation of formation of the column structure in **8** and its phase behavior (Col_{ro}: ordered rectangular columnar phase, Col_{oh}: ordered hexagonal columnar phase, Iso: isotropic liquid), and b) bent structure (front and side views) of **8'** calculated by AM1.

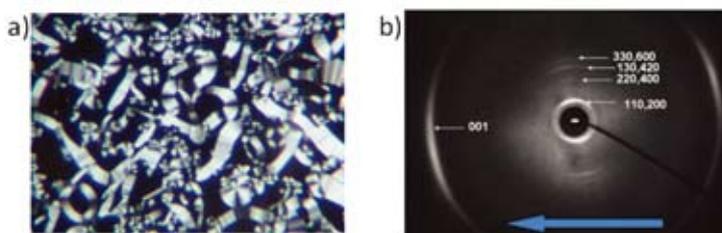


Figure 14. a) Polarized optical micrograph (POM) and b) the two-dimensional XRD profile (the arrow indicates the sheared direction) of **8**.

5. Application of Smectic Phases to Molecular Molding by Polymerization

As shown in Figure 15a, it is known that hexagonal columnar phases are useful for fabrication of molecular molds.¹⁷ Polymerization of a columnar structure possessing core molecules (or ions) at their central parts followed by removal of the core molecules (or ions) gives nano-porous materials. The materials have a rigid honeycomb structure and are useful for molecular recognition. On the other hand, it is difficult to fabricate molecular molds using smectic liquid crystal phases (Figure 15b), and removal of core molecules from the corresponding polymers causes a crush of the layer structure.

Nevertheless, we attempted to use smectic phases to fabricate molecular molds.¹⁸ As shown in Figure 16, supramolecule **9** has a dipyriddyethane molecule as the core molecule, and each of its terminals is connected with a *p*-alkoxybenzoic acid derivative by intermolecular hydrogen bonds. Two polymerizable substituents are introduced laterally to this benzoic acid derivative. We also synthesized a rod-like compound **PL** (an abbreviation of “pillar”) in which the molecular parts were connected covalently. Compound **9** exhibited a smectic A phase (Figure 16-micro photograph) in which the molecules have a multi-layered superstructure, and the pure compound (**9**: 100%) was photo-polymerized to give the corresponding polymer. However, as shown in Figure 17,

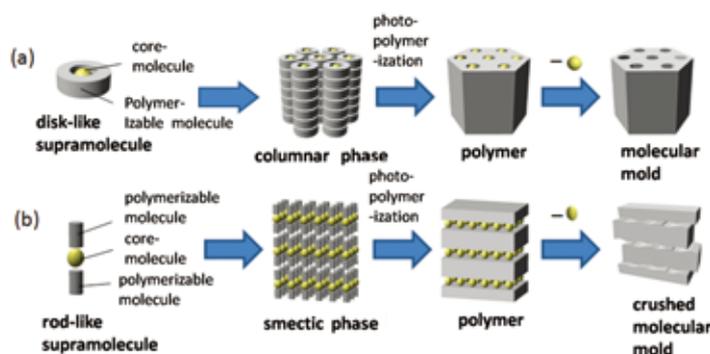


Figure 15. Fabrication of molecular molds using supramolecular compounds using a) hexagonal columnar phases and b) smectic phases.

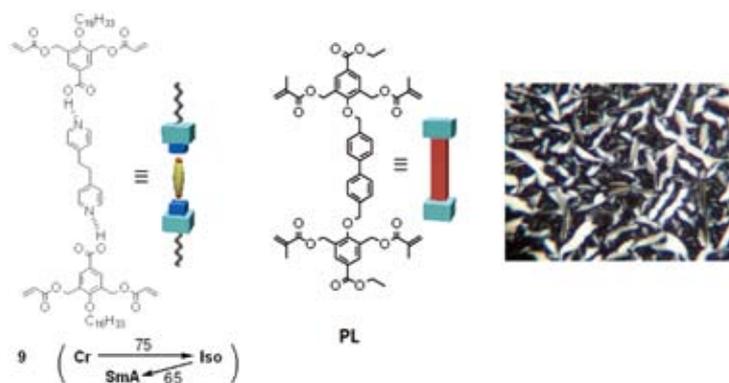


Figure 16. Structures of supramolecule **9** and pillar molecule **PL**. The microphotograph is the texture of **9** in the smectic A phase.

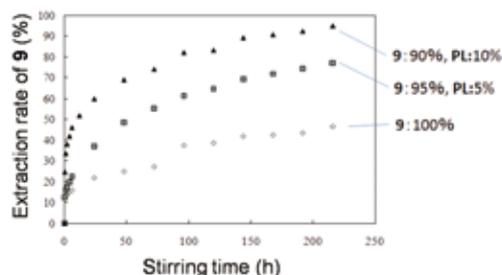


Figure 17. Plots of the amounts of dipyriddyethane extracted with 3M hydrochloric acid from the polymers obtained from the mixtures of **9** and **PL** (**9**/**PL** = 100:0, 95:5, and 90:10) against the stirring time at room temperature.

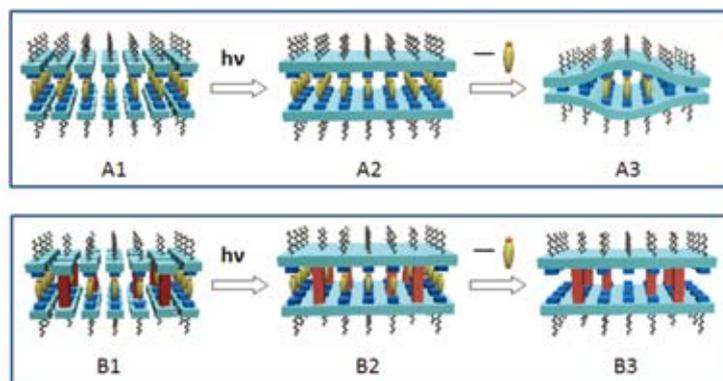


Figure 18. Process of photo-polymerization of **9** (A1→A2) and extraction of dipyridylethane (A2→A3), and that of photo-polymerization of **9+PL** (B1→B2) and extraction of dipyridylethane (B2→B3).

extraction of dipyridylethane from the obtained polymer with 3M hydrochloric acid proceeded slowly. Even after 216 hours, 50% of dipyridylethane remained in the polymer. It was assumed that the core molecules could not go outside because a crush of the layer structures occurred from the edge of the polymer sheets (Figure 18: A1→A2→A3). Then, we attempted to introduce **PL** molecules in the layers. With compound **9**, 5% and 10% of compound **PL** were mixed to give the corresponding mixtures, and the mixtures were photo-polymerized in their liquid crystal phase. In the extraction of the core molecules from the polymers obtained, 75% and 100% of core molecules were extracted, respectively, which was explained by the polymer not crashing after the extraction. Thus, it was confirmed that the superstructure of the smectic phases could be utilized for molecular molding by introduction of the pillar molecules. We would like to synthesize polymers possessing a high ability in molecular recognition by introduction of pillar molecules which interact with guest molecules.

6. In Conclusion

Twelve years have passed since I got the sheet of paper on which a liquid crystalline molecule was written. I have been studying liquid crystalline molecules possessing a strong lateral interaction. Introduction of a large interaction in the direction of the molecular short axis strongly destabilizes liquid crystal states, and in most of the cases the molecules do not show any liquid crystal phase. However, if I solve the problems, I can have many chances to find novel phenomena. And also I can greatly feel a sense of achievement. These days, I have one policy. "In my project, the simplest molecules possible should be used to achieve the purpose". Simple compounds are easily available, which is one of the merits. More significant merits are that achievement of the purpose with simple molecules gives a strong impact to many scientists and someone will use our molecules in their projects. Further, it is easy to explain mechanism of a novel phenomenon with simple molecules, and we can easily imagine its application.

So, I would like to continue syntheses of exotic and simple liquid-crystalline molecules and make useful molecules from them.

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[Specialties] Liquid-crystal Chemistry, Organic Synthesis, Organic Photochemistry, Construction of Nanostructures