

Development of Chiral Polymer Frameworks with Large-area Three-dimensional Molecular Ordering

(大面積で三次元的に分子配列した多孔性キラル高分子の開発)

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1. Introduction

When appropriately functionalized molecules are arranged in one-handed helices, they often display intriguing physical phenomena that never occur in centrosymmetric structures, as represented by second harmonic generation (SHG) and piezoelectricity. These helices would also give a clue to pursue unexplored predictions, including molecular solenoid effects. To explore these phenomena further, a key issue is to improve the quality of their output signals. For this purpose, the most straightforward approach is to orient the helices macroscopically so that mutual cancellation of signals is prevented. Although such hierarchical structures, realizing one-handed helicity and macroscopic orientation at the same time, are rarely obtained, their rational formation would become possible by using a framework with macroscopically oriented helical pores. If this framework serves as a scaffold for arraying various molecules in a macroscopically oriented helical structure by simple host-guest complexation, it should facilitate the exploration of the aforementioned phenomena. However, such a framework has not been developed so far. Even in the case of achiral pores, their macroscopic orientation remains a general challenge. For the present purpose, individual pores must be helical and capable of precisely positioning the incorporated molecules, which makes this challenge even greater.

With the aim of developing such frameworks, I focused on an advanced version of molecularly imprinted polymers prepared by the crosslinking of liquid crystals (LCs), and are now regarded as a new class of solid-state hosts. When a multicomponent LC composed of a polymerizable frame unit and a non-polymerizable template unit (for example, Fig. 1, i) is in situ crosslinked, the frame units are converted into a polymer framework, while the template units are noncovalently captured in the polymer framework and therefore are exchangeable with other molecules. As demonstrated, chiral pores are rationally constructed by using chiral template units.

Here I report an unprecedented type of polymer framework with macroscopically oriented helical pores, prepared by in situ crosslinking of a supramolecular LC preorganized in a magnetic field. This chiral liquid crystalline salt meets all requirements as the precursor of such framework, that is, multicomponent nature, polymerizability, orientability and helicity with controlled handedness. The resultant polymer framework serves as a versatile scaffold for arraying various molecules in a macroscopically oriented helical structure, thereby offering useful motifs for the exploration of the physical phenomena particular to noncentrosymmetric systems.

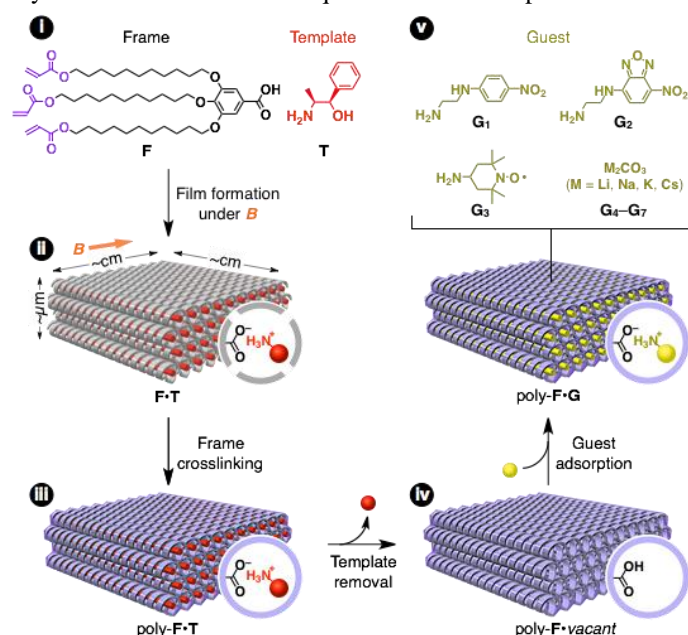


Figure 1. Macroscopically oriented polymer framework with helical pores by in situ crosslinking of a magnetically preorganized LC salt. (i) Molecular structure of the frame (polymerizable carboxylic acid, **F**) and template (enantiopure amine, **T**) units that self-assemble into a columnar LC salt. (ii) Processing of the salt (**F•T**) into a macroscopically oriented LC film in a magnetic field. (iii) In situ crosslinking of the LC film of **F•T** by radical polymerization to give a polymerized film consisting of poly-**F•T**. (iv) Desorption of **T** from the polymerized film of poly-**F•T** to give a guest-free film of poly-**F•vacant**. (v) Adsorption of guests **G**₁–**G**₇ by the guest-free film of poly-**F•vacant** to give a guest-exchanged film of poly-**F•G**. **B**: Magnetic field applied during the LC film-preparation process.

2. Experiment and Analysis

2-1. Synthesis of the macroscopically oriented polymer framework

The polymer framework is prepared with a supramolecular columnar LC material recently reported by our group. This consists of a polymerizable carboxylic acid that contains three flexible chains (frame, **F**) and an enantiopure amine (template, **T**). On mixing in equimolar amounts, these components form a salt (**F•T**) that exhibits a stable columnar LC mesophase. When **F•T** was slowly cooled from an isotropic molten state at 130 to 20°C, small, randomly oriented LC domains (~10 μm) were formed, as confirmed by polarized optical microscopy (POM; Fig. 2a). On the other hand, drop casting of its dichloromethane solution on a glass substrate produced relatively large LC domains, with a size of the order of millimetres and a characteristic crosshatched texture (Fig. 2b).

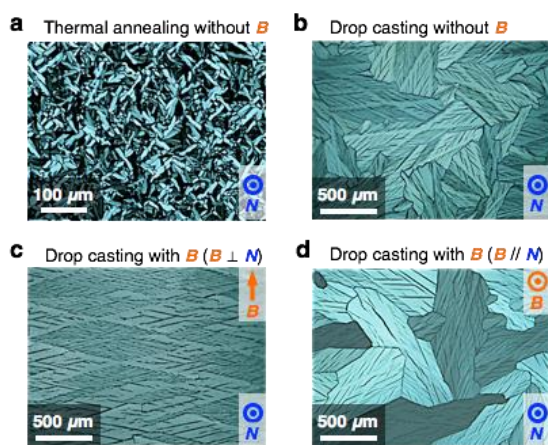


Figure 2. POM images of F•T under crossed Nicols. (a) LC film ($\sim 10 \mu\text{m}$ thick) of F•T processed by slow cooling ($-5 \text{ }^\circ\text{C min}^{-1}$) from an isotropic melt at 130 to $20 \text{ }^\circ\text{C}$ in the absence of a magnetic field. Scale bar, $100 \mu\text{m}$. (b–d) LC films ($\sim 10 \mu\text{m}$ thick) of F•T processed by drop casting of a dichloromethane solution on a glass substrate at $20 \text{ }^\circ\text{C}$: in the absence (b) and presence of a 10-T magnetic field oriented parallel (c) and perpendicular (d) to the substrate plane. Scale bar, $500 \mu\text{m}$.

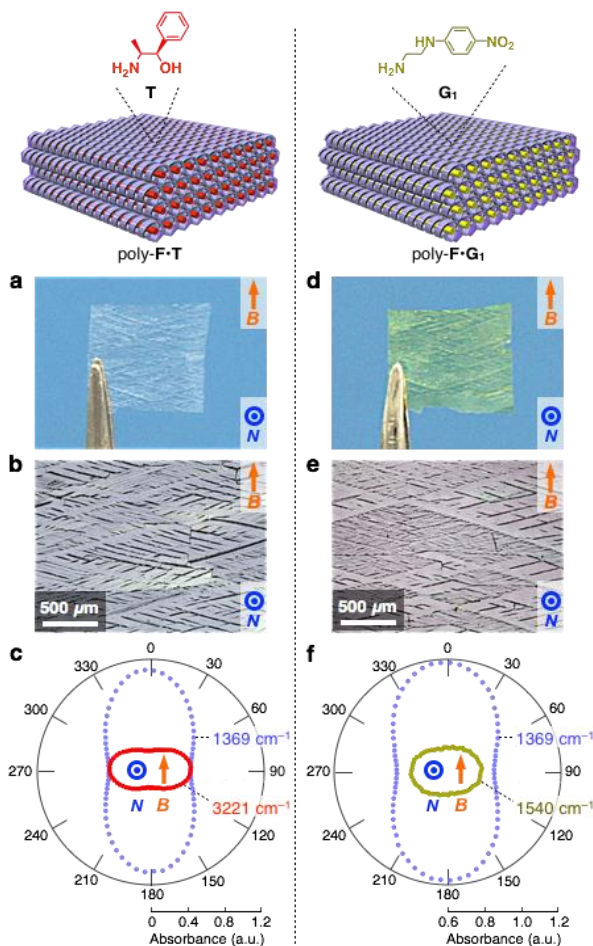


Figure 3. Properties of films with macroscopically oriented structures. (a–c) Film of poly-F•T ($\sim 10 \mu\text{m}$ thick) prepared by in situ crosslinking of the LC film of F•T with a magnetically oriented structure. (d–f) Film of poly-F•G₁ ($\sim 10 \mu\text{m}$ thick) prepared by the guest exchange of the film of poly-F•T with a magnetically oriented structure. Pictures (a,d), POM images under crossed Nicols (b,e) and polar plots of the infrared absorption as a function of the light-polarization angle (c,f). Scale bar, $500 \mu\text{m}$.

Interestingly, however, the application of a strong magnetic field during the drop-casting process resulted in perfectly controlled orientation of the LC domains over an $\sim 10\text{-cm}^2$ -size scale (Fig. 1, ii). For example, F•T (24.9 mg , $25 \mu\text{mol}$) in dichloromethane ($500 \mu\text{l}$) was cast on a glass substrate and slowly concentrated to dryness over 2 h at $20 \text{ }^\circ\text{C}$ in the presence of a 10-T magnetic field oriented parallel to the substrate plane. As shown in Fig. 2c, the resultant LC film exhibited rhombic patterns of multiple LC domains that aligned along the applied magnetic field to form a continuous two-dimensional (2D) array. When a 10-T magnetic field was directed perpendicular to the substrate plane, essentially no effect was brought on the orientation of the LC domains (Fig. 2d). These observations indicate that only the horizontal (in-plane) component of the magnetic field vector contributes to this magnetic orientation. For covalent fixation of the magnetically oriented structure, the LC film of F•T was then subjected to in situ crosslinking polymerization (Fig. 1, iii). To polymerize the acryloyl groups in F, γ -ray irradiation method can be operated without a radical initiator and is a promising method for preserving an organized structure. On irradiating the LC film with γ -ray (6.25 kGy h^{-1}) at $20 \text{ }^\circ\text{C}$ for 16 h , crosslinking polymerization proceeded quantitatively to convert the viscous fluidic F•T into an insoluble and non-meltable solid consisting of the salt of polymerized F (poly-F) and T (denoted hereafter as poly-F•T). This polymer film was flexible and freestanding, so that it was easily peeled off from the glass substrate (Fig. 3a).

2-2. Structural analysis of the framework

As observed in POM (Fig. 3b) or even by the naked eye (Fig. 3a), the crosshatched texture was extended over the entire region of the polymer film, suggesting that the crosslinking and the peel-off processes had no effect on the macroscopic orientation. When the polymer film was rotated in an in-plane manner, its POM showed a contrast every 45° , giving a dark image when the light-polarization angle with respect to the applied magnetic field was 0° or 90° . The polarized infrared absorption of the film also showed an apparent dependency on the polarization angle, in that the peaks at 1369cm^{-1} ($-\text{CO}_2^-$) and 3221cm^{-1} ($-\text{N}^+\text{H}_3$) became maximal at the polarization angle of 0° and 90° , respectively (Fig. 3c). From these observations, it is obvious that columnar aggregates of F and T, which are afforded by salt-pair formation between the $-\text{CO}_2\text{H}$ and $-\text{NH}_2$ groups, lie along the glass surface and are oriented perpendicular or parallel to the applied magnetic field.

As shown in Fig. 4 (top), the polymer film was exposed to a beam of X-rays from the directions perpendicular (through view) and in-plane (edge and end views) to the film surface to obtain three-dimensional (3D) structural information. In the wide-angle region of the 2D X-ray diffraction images, two types of diffractions characteristic of columnar LCs were observed: a diffuse halo (d -spacing, 4.4 \AA) due to the loose packing of the aliphatic chains (Fig. 4a–c, i) and a pair of obscure spots (d -spacing, 3.6 \AA) attributable to the stacking of the π -conjugated systems (Fig. 4a,b, ii). Because the diffractions from the π -

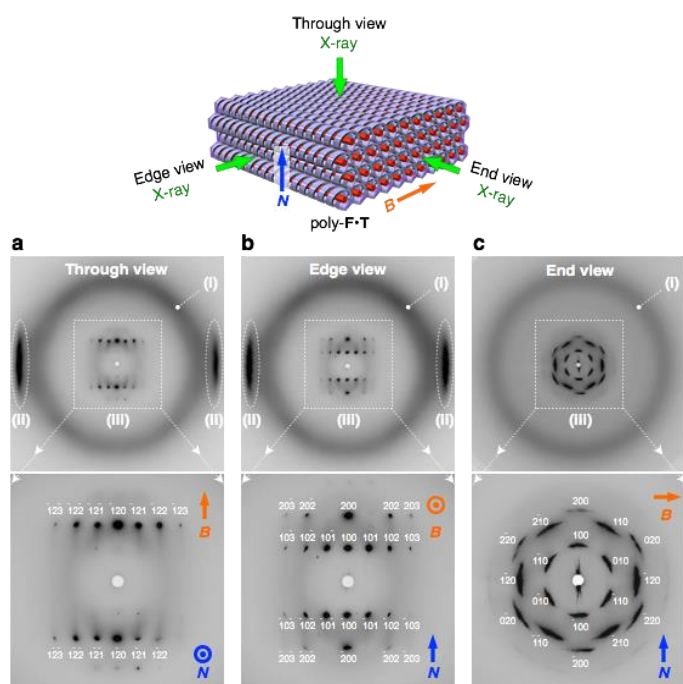


Figure 4. 2D X-ray diffraction images of a film of poly-F•T with a macroscopically oriented structure. (a) Through view image (X-ray//N, X-ray \perp B). (b) Edge view image (X-ray \perp N, X-ray//B). (c) End view image (X-ray \perp N, X-ray \perp B). (i), (ii) and (iii) highlight signals due to aliphatic chain packing, π -stacking and 3D lattice, respectively.

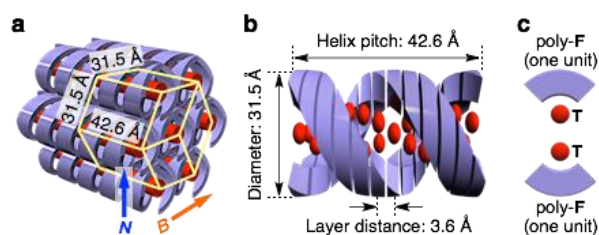


Figure 5. Schematic of the structure of poly-F•T. (a) Hexagonally packed helical columns (diameter, 31.5 Å) with structural periodicity along the column axis (distance, 42.6 Å) (b) Supramolecular duplex formed by the stacking of the repeating unit (shown in c). (c) Repeating unit consisting of two salt pairs of poly-F and T.

only defined the columns to orient within the substrate plane and did not restrict their in-plane rotation.

2-3. Use of the framework as a solid-state host

By immersing a film of poly-F•T in acidified ethanol at 20°C for 10 h, T can be quantitatively desorbed from the framework of poly-F (Fig. 1, iv), owing to the lack of covalent interactions between T and poly-F. The resultant film, which consisted exclusively of guest-free polymer framework (poly-F•vacant), showed infrared absorption characteristic of a free carboxyl acid ($-\text{CO}_2\text{H}$), while the absorption associated with the carboxylate ion ($-\text{CO}_2^-$) disappeared.

Because poly-F•vacant contains hollow pores featuring many $-\text{CO}_2\text{H}$ groups, the guest-free film readily incorporates various basic or cationic guest molecules G_1 – G_7 (Fig. 1, v). For example, when a film of poly-F•vacant was immersed at 20 °C for 8 h in a methanolic solution of an amine bearing a *p*-nitroaniline moiety (G_1), the film adsorbed ~ 0.9 equivalents of G_1 with respect to the $-\text{CO}_2\text{H}$ group content of the film. The resultant yellow film (Fig. 3d) retained its macroscopic orientation, as confirmed by POM (Fig. 3e). Amine G_2 bearing a fluorescent moiety and amine G_3 bearing a stabilized radical as well as alkali metal ions (G_4 – G_7) were also incorporated as guests in the polymer framework through salt-pair formation with retention of the macroscopic orientation.

As a representative example of a guest-exchanged film, that of poly-F• G_1 was investigated in more detail. In polarized infrared spectroscopy, its absorption at 1,369 cm^{-1} ($-\text{CO}_2^-$) and 1,540 cm^{-1} ($-\text{NO}_2$) was clearly dependent on the light-polarization angle (Fig. 3f), indicating that the molecular units of F and G_1 are anisotropically positioned in the macroscopically oriented helical pores. After incorporation of G_1 , the polymer

stacking appeared only in the equatorial region of the through and edge views, the π -conjugated systems in F•T are probably stacked in the direction perpendicular to the magnetic field.

A number of sharp spots appeared at regular intervals in the small-angle region (Fig. 4a–c, iii), unlike usual fluctuation because of the flexible, polydomain nature of the film, as exemplified by the radially broaden spots in Fig. 4c. To remove the effects of polydomain nature, a monodomain clump trimmed from the film was used instead, where much narrower spots were observed. Such a flatten conformation would facilitate the stacking of the salt pairs of F and T, as suggested by the diffraction due to π -stacking (Fig. 4a,b ii). In the LC structure of F•T, the salt pairs assemble in a helical array, most likely because of the steric hindrance of the long alkyl chains in F.

The structural model in Fig. 5 accords with the general tendency of π -conjugated systems to orient parallel to an applied magnetic field, and explains the mechanism underlying the present magnetic orientation. Given that an applied magnetic field orients the π -conjugated systems in individual molecules of F and T parallel to the field, it would generate a torque that orients their columnar aggregates perpendicular to the magnetic field. Simultaneously, the columns are induced to lie along the surface of the film, most likely because of the interaction of the columns' aliphatic side chains with the air interface during the drop-casting process. When the magnetic field is applied along the substrate plane, the magnetic and surface effects cooperate to produce a unidirectional orientation. This hypothesis is consistent with the observation that a magnetic field applied perpendicular to the substrate plane had no effect on the structural ordering (Fig. 2d), where both the magnetic and surface effects

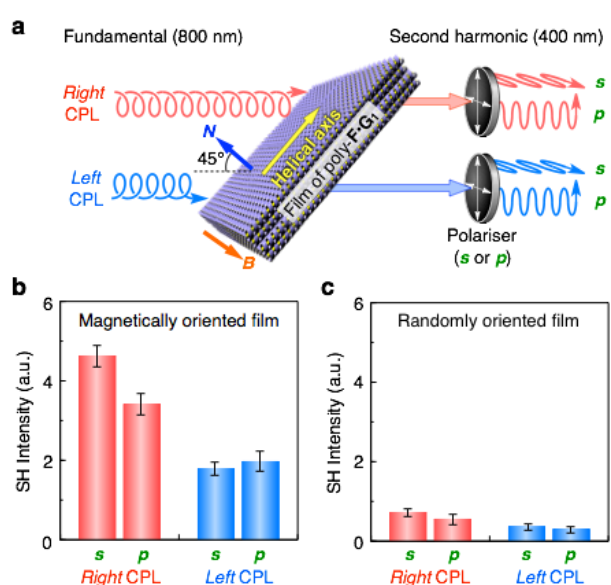


Figure 6. SHG circular dichroism measurement of films of poly-F•G₁. (a) Optical set-up. As a fundamental beam, right- (red) or left-handed (blue) CPL (800 nm wavelength) was incident at 45° to a film of poly-F•G₁ with magnetically oriented structure. The film was set so that the direction of the magnetic field that was applied during the LC film-formation process was perpendicular to the incident plane, that is, the helical axes of the columnar objects were parallel to the incident plane. Generated frequency-doubled light (400 nm wavelength) was detected from the transmitted direction by using an s- or p-analyser. (b,c) SHG output power for a film of poly-F•G₁ with a magnetically oriented structure (b) and for an analogous film with a randomly oriented structure (c). Each error bar represents the s.d. of 100 replicate measurements.

contribution of polar structures. Contrary to them, our polymer framework with a chiral and apolar space group (P6₁22 or P6₅22) would afford NLO output genuinely because of chirality, which is suitable for pursuing nonlinear phenomena in chiral architectures. Furthermore, the macroscopic orientation of poly-F would be expected to have positive effects on the NLO output because the NLO signals generated from the ordered structure should be less prone to mutual cancellation and therefore coherent.

To confirm this possibility, I measured the SHG of the film of poly-F•G₁ (Fig. 6a). Circularly polarized light (CPL) was used with right- or left-handedness as a fundamental beam, so that it can be determined, independently of any effect of birefringence, whether the origin of the SHG was the chiral arrangement induced by the polymer framework or whether it arose from coincidental polar ordering. To detect the SHG circular dichroism clearly, the incident angle was set to 45°, and the s- and p-polarized contents of the SHG output were separately monitored. When right-handed CPL (wavelength, 800 nm) was irradiated to a 5-μm-thick film of poly-F•G₁ with a magnetically oriented structure (Fig. 6a, red), strong SHG output was observed for both of the s- and p-polarized contents (Fig. 6b, red). On switching the handedness of the CPL from right to left (Fig. 6a, blue), the intensity of the SHG reduced by half (Fig. 6b, blue), proving that the SHG observed here is because of the chiral arrangement of G₁. As I had conjectured, the macroscopic orientation of the framework had a significant effect on the SHG output. Indeed, the SHG intensity of the film with magnetically oriented structure (Fig. 6b) was seven times greater than that of an analogous 5-μm-thick film with a randomly oriented structure (Fig. 6c).

3. Conclusion and Perspectives

The new polymer framework (poly-F), prepared by in situ crosslinking of a chiral supramolecular LC salt (F•T) preorganized in a magnetic field (Fig. 1), is the first porous material that realizes helicity with controlled handedness and macroscopic orientation at the same time. The framework, capable of incorporating various basic or cationic guest molecules and restricting their positions, is expected to serve as a ‘universal’ scaffold for arraying molecules into a helical and macroscopically oriented structure. The resulting arrangement of the guest molecules might be suitable for inducing molecular events to proceed in a directionally controlled and mutually correlated manner, as exemplified by the SHG of a NLO chromophore (G₁) demonstrated in this work. Further potential applications of our framework include CPL-emitting devices, piezoelectric materials, chiral magnets, anisotropic ion-conductive materials or membranes for chiral separation.

framework retained its hexagonal columnar packing, and, moreover, recovered the periodicity of helical pitch. In fact, the 2D X-ray diffraction patterns of poly-F•G₁ were quite similar to those of poly-F•T (Fig. 4) for all three views. In addition, lattice parameters of poly-F•G₁ (column diameter = 31.4 Å, helical pitch = 42.8 Å) were essentially identical to those of poly-F•T (column diameter = 31.5 Å, helical pitch = 42.6 Å), despite the different molecular shapes of G₁ and T. Such consistency in lattice parameters suggests that a fundamental skeleton of the helical pores might be preserved in poly-F even after the helical pitch disordering because of the desorption of T. It is probable that molecules of G₁ filled the spaces originally occupied by T molecules, thereby reducing the structural strain in the polymer framework and recovering the helical pitch. From these observations, I also deduced that the molecules of G₁ in the polymer framework were present in a helical arrangement, as in the case of T. In this case, a chiral structure emerged from achiral components (F and G₁) because of the chiral template effect of T.

Owing to their push-pull-substituted aromatic systems, p-nitroaniline derivatives such as G₁ are known to exhibit the second-order nonlinear optical (NLO) properties, when they are arrayed in a noncentrosymmetric (= polar, chiral or both) arrangement. Because the molecules of G₁ confined in poly-F are likely to align in helical arrays, as described above, they potentially show second-order NLO properties. Although there have been reported several host systems that induce the NLO output of chromophore guests, most of them contain the