

## 論文の内容の要旨

論文題目 Molecular Design of Thiophene-based Helical Architectures

(チオフェンをモチーフとするらせん構造の分子設計)

氏名 肖琦

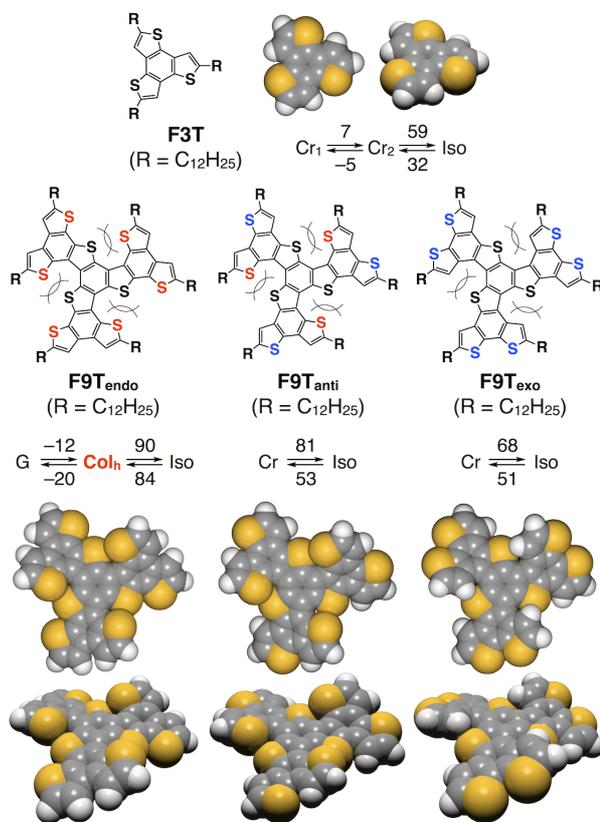
### Introductions of Helical Polymers

In nature, there are a large number of helical biomolecules. The most famous examples are right-handed  $\alpha$ -helix for proteins and the right-handed double stranded helix for DNA. Meanwhile, according to the development of organic and polymer synthesis or supramolecular self-assembling, numerous artificial helical structures have been well studied. Because of their special conformation and optical activity, chemists have been challenged to develop not only to mimic biological helices and functions but also for their potential applications in materials science, such as chiral recognition, asymmetric synthesis, and others in material science.

### Propeller-shaped Fused Oligothiophenes: Helical Architectures from Supramolecular Self-assembly.

We report **F9T<sub>endo</sub>**, **F9T<sub>anti</sub>**, and **F9T<sub>exo</sub>** (Figure 1) whose regioisomeric aromatic cores comprise 9 nonlinearly connected fused oligothiophene units. We initially thought that these aromatic cores would adopt a disk shape appropriate for  $\pi$ -stacking and envisioned that **F9Ts** might self-assemble into columnar liquid crystalline (LC) materials with the help of their 6 dodecyl side chains. However, to our surprise, only **F9T<sub>endo</sub>** forms a columnar LC assembly. We then noticed that the aromatic cores of **F9Ts** are not planar but adopt a  $C_3$ -symmetric propeller shape due to a considerable steric repulsion among proximal sulfur atoms.

In differential scanning calorimetry (Figure 1), **F9T<sub>anti</sub>** and **F9T<sub>exo</sub>** upon heating only showed a transition from a crystalline phase to an isotropic melt. However, **F9T<sub>endo</sub>**, in contrast, displayed a LC mesophase over a wide temperature range from  $-12$  to  $90$  °C (from  $84$  to  $-20$  °C upon cooling). Its crossed polarized optical microscope (POM) image showed a birefringent dendritic texture typical of columnar LC materials. In fact, upon exposure to a synchrotron radiation X-ray beam, **F9T<sub>endo</sub>** in the LC state at  $30$  °C clearly displayed a set of diffraction peaks at, *e.g.*,  $q = 2.19, 3.81, \text{ and } 4.39 \text{ nm}^{-1}$  indexed as 100, 110, and 200 planes, respectively, of a hexagonal columnar (Col<sub>h</sub>) lattice with a lattice parameter  $a$  (intercolumnar distance) of  $3.31 \text{ nm}$ . Noteworthy, the



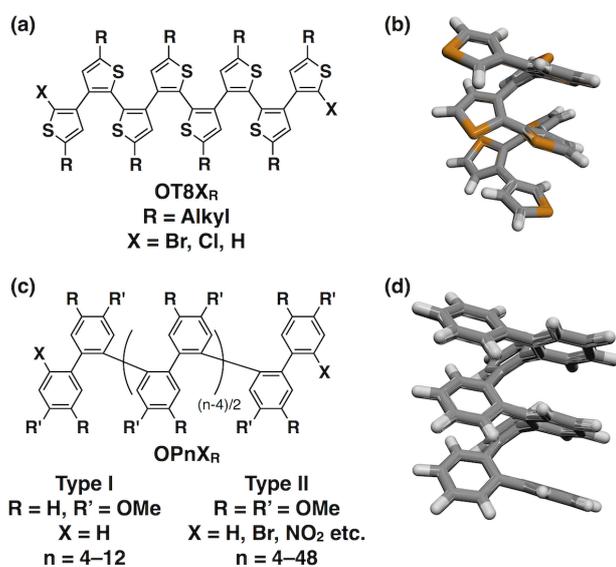
**Figure 1.** Chemical structures and computer-generated models of **F3T**, **F9T<sub>endo</sub>**, **F9T<sub>anti</sub>**, and **F9T<sub>exo</sub>**, and their phase behaviors with transition temperatures ( $^{\circ}C$ ). Structural optimizations were performed with DFT at the B3LYP/6-31G(d) level.

purpose of obtaining a solid support for this geometrical feature, a sheared LC film of **F9T<sub>endo</sub>** was prepared, whose brightness in POM showed an angle-dependent periodic change. Furthermore, this sheared LC film, in 2D WAXD analysis, gave the diffraction of  $hkl = (001)$  along the sheared direction, and hexagonal patterns as  $hkl = (100)$  and  $(110)$  perpendicular to the sheared direction. These features allowed us to confirm that the LC columns in the film are oriented along the sheared direction. Then, typical off-meridional diffractions with the tilt angles of  $\pm 20^{\circ}$  was observed. This result demonstrates that the columnar assembly of **F9T<sub>endo</sub>** adopts a helical geometry along the columnar axis. Taking into account the  $C_3$  symmetry of **F9T<sub>endo</sub>**, the helical pitch of the LC columns can be estimated as 4.04 nm. Hence, the dihedral angle of two adjacent core units in a single column is calculated as  $32.5^{\circ}$ . Thus, in a stacked dimer model of **F9T<sub>endo</sub>**, if the upper core is positioned with a dihedral angle of  $32.5^{\circ}$  onto the lower

XRD pattern also displayed a distinct diffraction at  $q = 17.3 \text{ nm}^{-1}$  with lattice parameter  $c$  of 0.364 nm, assignable to the stacking periodicity. Why does the assembling behavior of **F9T<sub>endo</sub>** differ from those of other two regioisomers, despite the fact that no remarkable difference lies in their optical and electrochemical properties? Although this was a puzzling issue for us, we found that **F9T<sub>endo</sub>** can take full advantage of S–S interactions for columnar stacking. A clue to solve this issue was given by a particular diffraction peak at  $q = 4.95 \text{ nm}^{-1}$  indicative of the presence of a long-range periodic structure. As described already, the  $\pi$ -stacked columns of **F9T<sub>endo</sub>** adopt a helical chirality. For the

core, three sets of intermolecular S–S contacts are simultaneously made possible. Similar but certainly much weaker S–S contacts are expected for **F9T<sub>anti</sub>**, whereas no such interactions are available for **F9T<sub>exo</sub>**. In accord with this consideration, soft-crystalline **F9T<sub>anti</sub>** actually showed a weak diffraction peak at  $q = 16.7 \text{ nm}^{-1}$  ( $d = 0.376 \text{ nm}$ ) assignable to the stacking distance of the core units.

## 2,2':3,3' Linked Oligothiophenes: A Stable “Rigidly Locked” Aromatic Foldamer

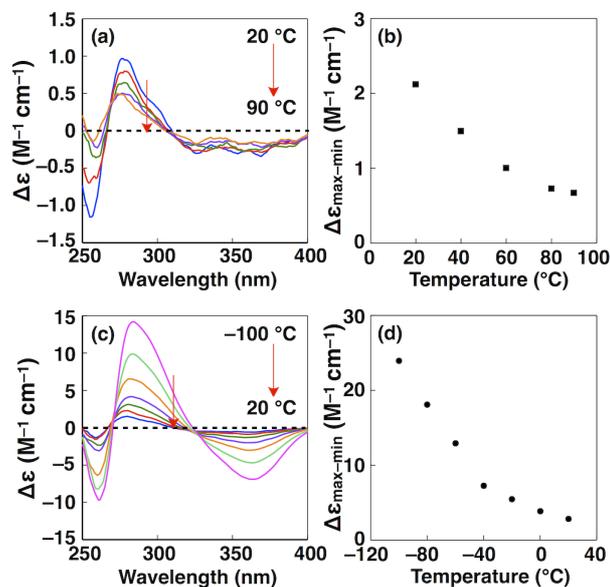


**Figure 2.** Structures of (a) 2,2':3,3'-linked oligothiophenes and (c) reported *ortho*-phenylenes. Helical structure of (b) 2,2':3,3'-linked oligothiophenes and (d) reported *ortho*-phenylenes.

*Ortho*-phenylenes, is a family of novel foldamer with perfect 3<sub>1</sub> helix, and has been well studied by Hartley (Figure 2c, Type I), Aida (Figure 2c, Type II) and co-workers. Because of heavily angled aromatic connections, these molecules showed special properties on conjugation, redox behavior, chiral inversion, and solvent effect. They concluded helix of *ortho*-phenylenes is very dynamic. Only in certain condition, it could maintain helical geometries, which differed from the expectation from the steric structures. An analogue structure with thiophene units was just preliminary researched by

Marsella on a crystalline analysis of hexamer with Cl as its substituted groups from step by step Pd-catalyzed coupling. It is still quite challenging for further discovery on longer oligomers and their helical properties.

As an inspiration from Cu (II) oxidative coupling between the 2,2' positions on thiophene rings, we started investigation from a 3,3' linked thiophene dimer. After a one-pot reaction of oxidative coupling and halogen substitution with copper (II) salt, unpredictable octamers (Figure 2a) with two terminal halogens were selectively isolated by size exclusion chromatography (SEC). Whenever the length of side chains or the counter ions of copper salts changed, the yields of octamers were almost constant in 20%. If these 2,2':3,3' linked oligothiophenes have similar helical structures as the *ortho*-phenylenes, all the R groups should toward outside to low down the energy, and



**Figure 3.** Temperature dependent CD spectra of **OT8BrC5\*** in (a) dioxane from 20 to 90 °C, (b) THF from -100 to 20 °C. (c) (d) Plots of the differential values of the maxima and minima molar circular dichroism  $\Delta\epsilon$  with temperatures. Isothermal-holding at each temperature for 10 min.

conformation, and its CD spectra was correlated to the CD of chiral biphenyls, as its analogue. The chirality of **OT2HC5\*** allowed us to get enantiomeric excess (*ee*) of **OT8BrC5\*** by the  $CuBr_2$  oxidative coupling. After the purification, we found it showed clear, stable although low CD signals. The shape of the curve is very similar with the *ortho*-phenylenes, but we did not observe the time-dependent decay of the CD intensity of chiral racemization. The chiral side chains induced the chirality of the helical, as we expected. The low intensity of the induced CD signals could be concluded as the very close energy levels of two helicity, even with the distinguishing effect of chiral chains. Finally, we checked the CD intensity (Figure 3) from 20 to 90 °C in dioxane and -100 to 20 °C in THF, respectively. The obvious decreasing of Cotton effects by heating. The shape of the curves did not change and could show the high stability of its folded helical structure. The intensity change of the CD signals is rapid, without notable time effect. From this result, we could summarize that unfolding dynamic to random coil species is prohibited, but the helical inversion is extremely fast.

aromatic thiophene units will stack heavily. With the long alkyl chains, these compounds showed highly fluidity. In contrast, methyl-substituted compounds were solid in room temperature. In addition, the Br-terminated compounds could easily convert to H-terminated ones in the strong base condition, such as *t*-BuLi.

We focused on compound **OT8BrC5\*** and conducted the circular dichroism (CD) spectroscopy. This octamer was synthesized from **OT2HC5\*** with (*S*)-2-methylbutyl as its side chains. **OT2HC5\*** is an axially chiral molecule with the rotation around the single bond between two thiophene rings. Thanks to the chiral chains, it showed stable chiral