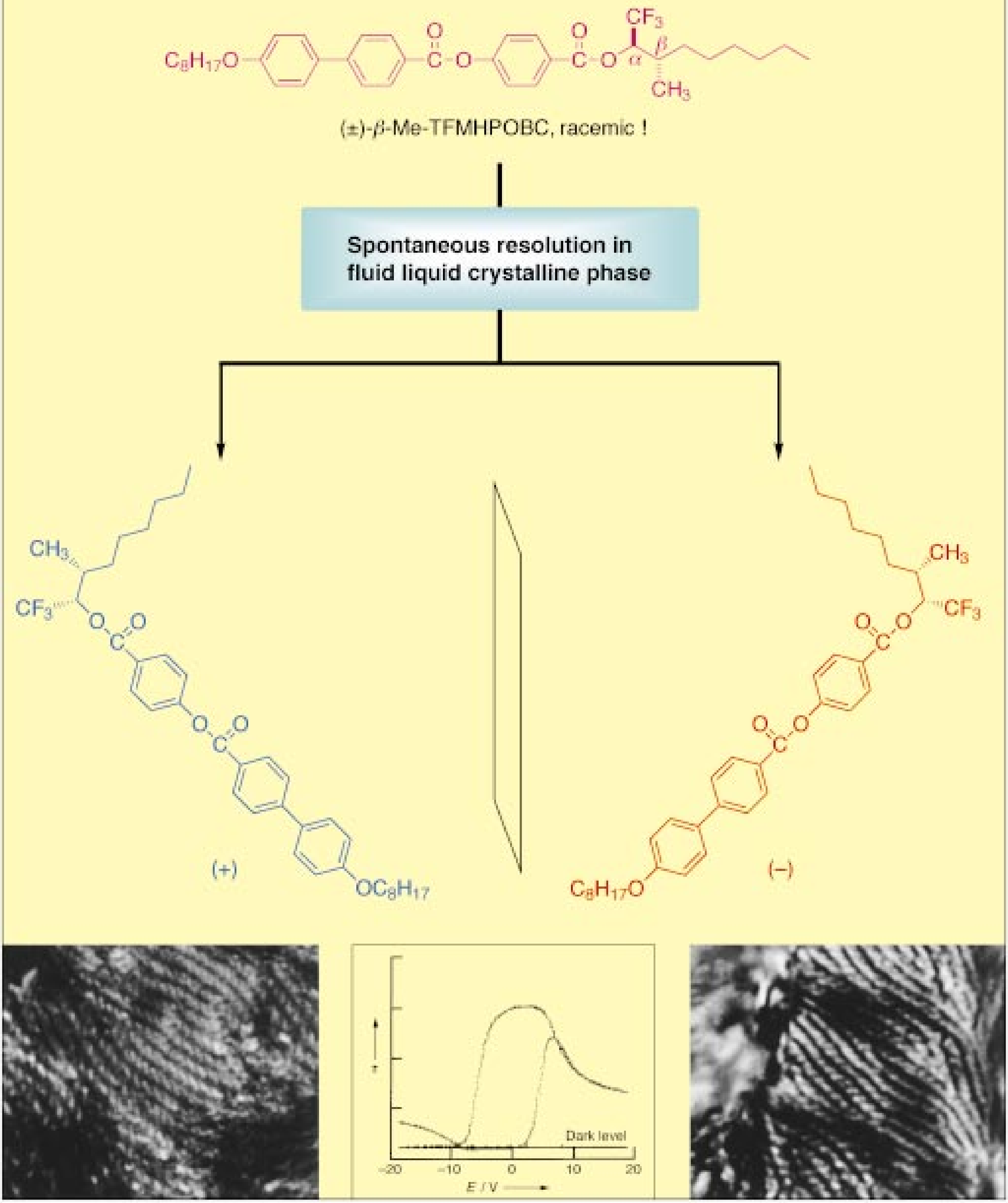
About 150 years ago, Pasteur found that crystals of “acide racemique” were spontaneously resolved into two enantiomeric forms. However, spontaneous resolution is rather unusual in particular in fluid systems such as liquid crystals owing to thermal fluctuations and/or molecular diffusion. Racemic β-Me-TFMHPOBC exhibits an electrooptic response and forms domains with stripes, which themselves display fine stripes. These fine stripes are tilted in two different directions with respect to the primary stripes, which indicates spontaneous resolution into a “three-dimensional conglomerate” in fluid condensed matter! Details are reported by Mikami et al. on the following pages.



Spontaneous Enantiomeric Resolution in a Fluid Smectic Phase of a Racemate

Yoichi Takanishi, Hideo Takezoe,* Yoshiichi Suzuki, Ichiro Kobayashi, Tomoko Yajima, Masahiro Terada, and Koichi Mikami*

Pasteur found 150 years ago that crystals of a sodium ammonium salt of “acide racemique” (sodium ammonium tartrate tetrahydrate) were spontaneously resolved into two enantiomorphous forms.[1] Pasteur’s finding initiated the concept of molecular dissymmetry in nature.[2] Inspite of extensive effort, no one has succeeded in observing the same phenomenon in a fluid phase rather than in a static crystalline phase.[3] We report here the spontaneous resolution of a racemic CF_3-containing liquid crystalline molecule, (R^*,S^*)-β-Me-TFMHPOBC (Figure 1), with a large spontaneous polarization (P_s) into a three-dimensional conglomerate. This is caused by accurate enantiomeric discrimination[4, 5] of the racemate by taking advantage of the two stereogenic centers.

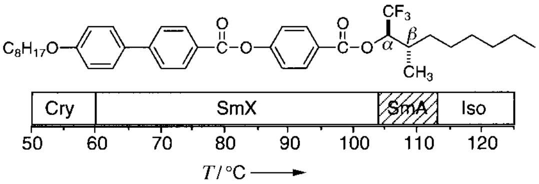


Figure 1. The structure of the *unlike* diastereomer (R^*,S^*)-β-Me-TFMHPOBC and the phase sequence upon heating. The material was sandwiched between glass plates to prepare a 2.7 µm thick homogeneously aligned cell by rubbing. Cry = crystalline, Sm = smectic, Iso = isotropic.

A number of compounds show the SmC phase, where molecules tilt with respect to the layer normal. If the system is chiral, it has C_2 symmetry with the twofold axis normal to the molecular tilting plane, so that a spontaneous polarization appears along this direction.[6] In this ferroelectric phase, molecules can be switched through ferroelectric interaction with an applied electric field. Even in an antiferroelectric phase where molecules in adjacent layers tilt in opposite directions and no net polarization exists,[7] the electrooptic switching occurs associated with the field-induced antiferroelectric to ferroelectric phase transition.[8] When the system is racemic, however, enantiomeric *R* and *S* molecules are completely mixed in each smectic layer. Therefore, the racemate has, in principle, no net spontaneous polarization in a layer and shows no significant electrooptic response, both in SmC and SmC_A.

Among antiferroelectric liquid crystals, α-methyl-substituted MHPOBC and the α-trifluoromethyl analogue TFMHPOBC (the β-methyl-substituted compound is shown in Figure 1), with larger P_s, have been extensively studied[9] because of potential application to electrooptic devices such as liquid crystalline displays (LCDs).[10] However, the racemic composition of MHPOBC or TFMHPOBC with a single stereogenic center did not show any significant electrooptic response. In sharp contrast, the (R^*,S^*)-β-Me-TFMHPOBC[11] analogues (Figure 1) exhibit distinct electrooptic switching even in their racemic composition, suggesting spontaneous enantiomeric resolution.

Figure 2a shows the electrooptic response observed in a homogeneous cell. The micrographs under the application of direct current (DC) fields of +3 and −3 V are given in

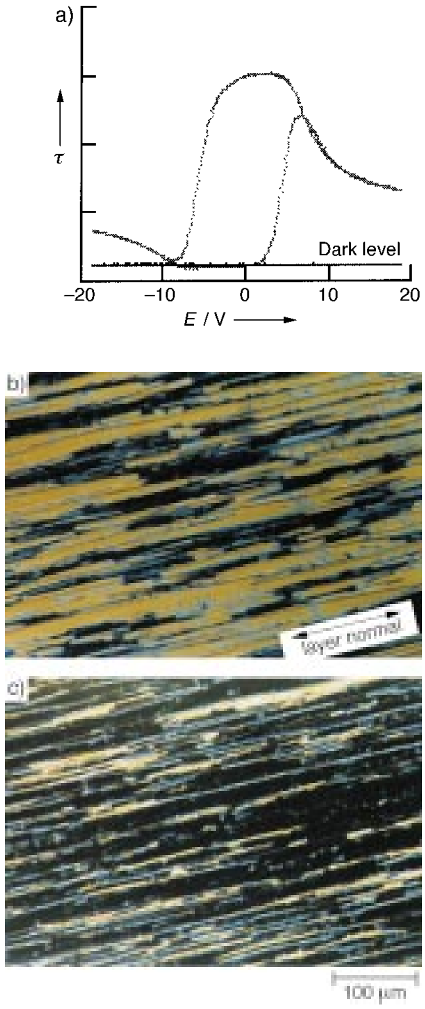


Figure 2. a) Optical transmittance τ (given in arbitrary units) versus applied triangular-wave electric field E at $T = 90\,^\circ C$. The electrooptic response was measured by applying a 1-Hz triangular-wave electric field to the cell under the crossed polarizers so that one of the uniform domains becomes dark. b), c) Microphotographs of the textures of the 2.7 µm thick homogeneous cell under the application of electric fields of −1.1 and +1.1 V µm^{-1}, respectively.

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Figures 2b and 2c, respectively. Generally, in the SmC phase of achiral or racemic compounds, molecules respond to a field only through dielectric interaction at high field, but no ferroelectric switching occurs, as mentioned above. Quite surprisingly, however, ferroelectric switching is observed in the cell of a racemic mixture (Figures 2b and 2c); uniform domains partially grow as they corrode the others. The brightness of these domains switched upon reversal of the field. With a further increase in the field, molecules rotated due to the dielectric anisotropy, changing the extinction normal to the smectic layer. This result clearly indicates that partial chiral resolution occurs and *R*,*S* and *S*,*R* molecules form their enantiomeric domains. We also detected a slight spontaneous polarization, though less than 10^{-2} nC cm^{-2} by the reverse field method.[12] This kind of obvious switching was not observed in racemic MHPOBC and TFMHPOBC with a single stereogenic center.

The second piece of evidence for enantiomeric separation was provided by the observed texture of a homeotropically aligned cell. In the racemic mixture of β-Me-TFMHPOBC, periodic stripe textures appear in addition to the normal schlieren texture (Figure 3). In this stripe, fine stripes with a smaller periodicity were also observed in each primary stripe. This fine stripe was tilted with respect to the primary stripes, clockwise in some regions (Figure 4a) and counterclockwise in others (Figure 4b), suggesting two enantiomeric domains.

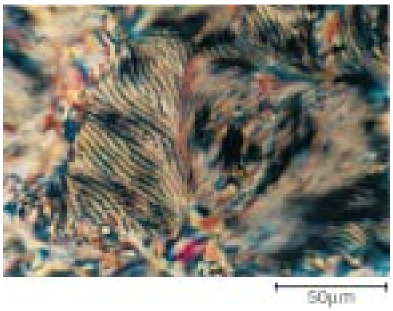

Figure 3. Microphotograph of a 25 µm thick homeotropically aligned cell in which the smectic layer is parallel to the substrate. The racemate of β-Me-TFMHPOBC exhibits periodic stripe textures; fine stripes with a smaller periodicity exist in each primary stripe. These fine stripes were tilted with respect to the primary stripes.

This texture is quite similar to that observed in an enantiopure MHPOBC and other ferroelectric liquid crystal compounds from Gorecka et al.[13] and Glogarova et al.[14] They reported that this pattern appears due to the in-plane director modulation connected with the unwinding of the helix, and that the tilting sense of the secondary stripes depends on the chirality. Therefore the texture observed in the present materials clearly indicates that enantiomeric domains segregate from the racemate. Indeed, these two domains show the opposite CD curves in the microscopic circular dichroism spectrum for the $10 \times 10 \mu m^2$ square of the enantiomeric domains in the homeotropically aligned cell (Figure 4, right).

Let us finally consider the reason why this enantiomeric resolution, which no one had observed so far, was detected in the present racemate. The important factor might be the difference of discrimination energy of the enantiomers; the conformation at the double stereogenic part of the molecule is more fixed in the bent conformation,[15] as compared with that of other molecules with a single stereogenic center such as MHPOBC and TFMHPOBC. Thus, the double stereogenic part brings about the spontaneous enantiomeric resolution in the present case. Actually, the racemic liquid crystal for (*S**,*S**)-β-Me-TFMHPOBC analogues[11] also exhibits electrooptic response, suggesting enantiomeric resolution. A similar fringe pattern was observed even in racemic mixtures of molecules such as MHPOBC and TFMHPOBC with a single stereogenic center, though the stability and sharpness of the fringes are less than those in the diastereomer. Thus the ease of spontaneous resolution is in the following order: double stereogenic β-Me-TFMHPOBC > single stereogenic TFMHPOBC > MHPOBC.

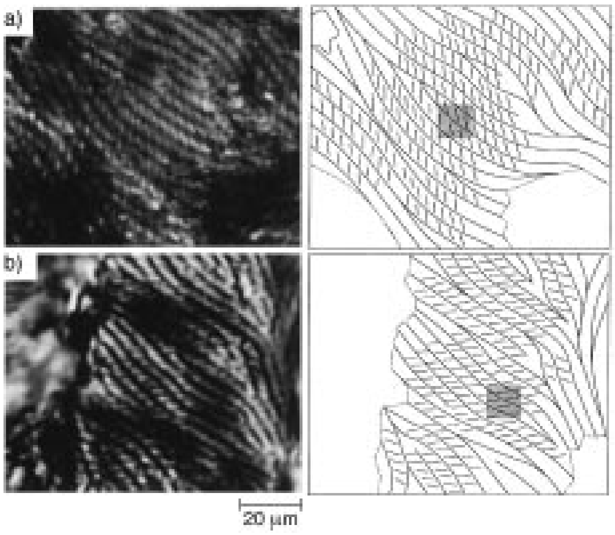

Figure 4. Microphotographs (left) of the stripe texture with the secondary stripe (shown schematically on the right). These fine stripes were tilted with respect to the primary stripes. The tilting sense was clockwise in some regions (a) and counterclockwise in others (b).

In conclusion, spontaneous resolution was discovered in a fluid liquid crystal phase by electrooptic measurement and texture observation. In the electrooptic measurement, partial domain switching was observed, suggesting that molecules with the same chirality partially self-assemble to form homochiral domains. In addition, stripe textures which have tilted secondary stripes with opposite tilting senses were also observed. Since the two tilting senses correspond to the chiral senses of enantiomers, it is concluded that enantiomeric domains separately coexist.

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Towards Sixfold Functionalization of Buckminsterfullerene (C_{60}) at Fully Addressable Octahedral Sites**

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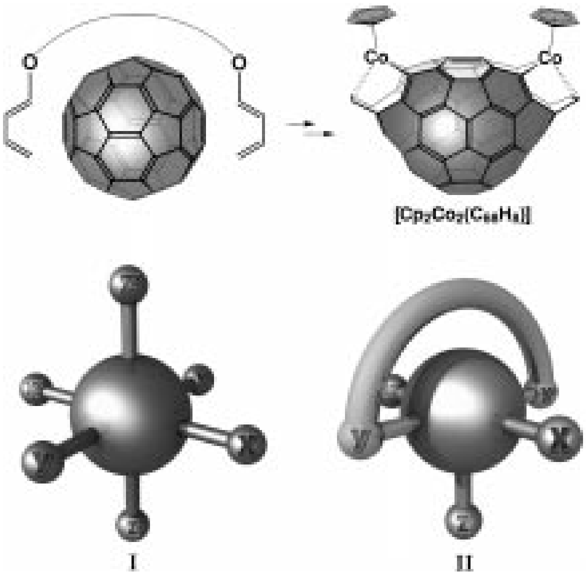

In the context of our fullerene opening strategies,[1] a relatively efficient method of functionalizing the opposite double bonds of C_{60} (*trans*-1 positions) by a twofold Diels–Alder reaction was required as a way to access the bis-cobalt complex $[Cp_2Co_2(C_{68}H_8)]$. Within a broader context we have been interested in the development of selective C_{60}-functionalization reactions that provide access to unusual multifunctional molecules with spatially defined addends.[1–5] Most current methods are confronted with the formation of regioisomeric by-products, coupled with the difficulty of maintaining stereochemical control throughout the addition steps. Hence, methods providing complete control of the degree and regiochemistry of additions on C_{60}, as well as the type of addends, are still needed for the construction of highly organized three-dimensional scaffolds (for example, **I**, where X, X′, Y, Y′, Z, Z′ are all different groups). The method reported here gives rapid access to a variety of multiple adducts in high yields from a tethered *trans*-1 bisadduct **3a** (see Scheme 1). Bisadduct **3a** has temporary directing moieties that address reactants to only three sequential sites of an octahedral scaffold by exploiting steric and electronic effects (**II**, addends X, Z, X′). The trisadducts **5a**, **b** and **13**, and the

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