

## 論文の内容の要旨

### Anisotropic Electrical Materials based on Triphenylene-cored Discotic Columnar Liquid Crystals

(トリフェニレン誘導体ディスコティックコラムナー液晶を用いた異方性電子材料の開発)

李 廷湖

## INTRODUCTION

As soft electrical materials, the anisotropic carrier mobility of discotic liquid crystals (DLCs) along their  $\pi$ - $\pi$  columns is promising very much as the components of various organic semi-conducting materials. The  $\pi$ - $\pi$  stacked aromatic cores act as “conducting wires”, whilst the peripheral chains act as “insulators”. This allows quasi one-dimensional carrier mobility, which is a desirable state for various semi-conducting applications, such as organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs) or organic photovoltaic cells (OPVs). For those applications, one dimensional charge transport in a macro-length scale is essential, so the arrangement control of DLCs is a crucial issue.

The scope of this philosophy doctoral thesis is the preparation, characterization, and application of novel soft electrical materials based on triphenylene (TP)-cored DLCs. The focus is mainly about the control of their arrangement in a certain direction in a macro-length scale for anisotropic electrical material development. The research includes 1) the hybridization of DLCs with carbon nanotubes (CNTs), and 2) the formation of aligned double layers composed DLCs. Throughout these investigations, this research will suggest new strategies for DLCs towards anisotropic electrical material development.

## SECTION I

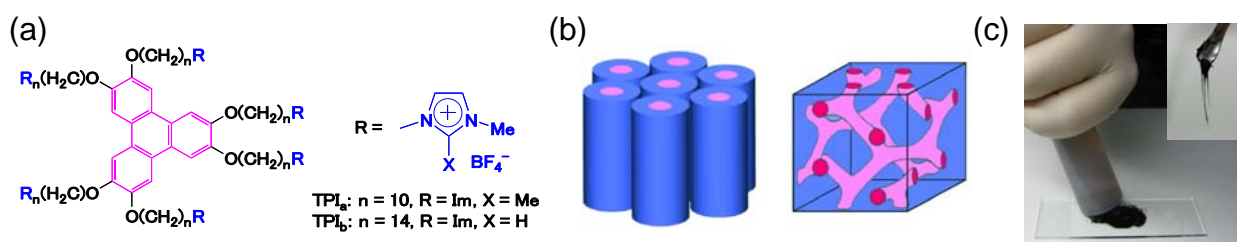
A variety of soft electrical conductors have been developed by doping CNTs into organic and polymeric materials, where better electrical properties are realized by dispersion of a larger amount of CNTs. Recently, LC materials attract increasing attention for hybridization with CNTs, as LC materials have the potential to orient CNTs for anisotropic electrical conduction. However, the loading levels of CNTs are only as small as 0.01 wt%. Very recently, TP derivative DLCs also have been reported to orient CNTs. However, due to their rather low miscibility with pristine CNTs, the use of CNTs covalently modified with TP was essential.

Herein the section 1, TP derivatives bearing six imidazolium ion pendants (TPI<sub>a</sub> and TPI<sub>b</sub>, **Figure 1a**) serve as excellent dispersants for pristine single-walled CNTs (SWNTs). The resultant composite materials can maintain their LC properties up to the SWNT content of about 8 wt%, which is 2–3 orders of magnitude greater than those reported previously. Of further interest, the ILC composites, when sheared, display anisotropic conducting properties, as SWNTs are oriented along the shear direction.

In 2003, our group reported that imidazolium ion-based ionic liquids, when being ground with SWNTs, are transformed into physical gels (bucky gels), where SWNTs are highly dispersed by a  $\pi$ -cation/ $\pi$ -electronic interaction and eventually form a 3D network structure associated with an interionic interaction of ionic liquids. As reported previously, TPI<sub>a</sub> and TPI<sub>b</sub> utilized for the present

study assemble into hexagonal columnar (134–188 °C on cooling; **Figure 1b**) and cubic (221–188 °C on cooling; **Figure 1b**) mesophases, respectively, over a wide temperature range, including room temperature.

As a typical example of the hybridization of TPIs with SWNTs, pristine HiPco SWNTs were added at 150 °C to TPI<sub>a</sub> (isotropic melt) with a SWNT content of 5 wt%, and the mixture was ground with a pestle for 30 min, whereupon it turned to a viscous black paste (**Figure 1c**). As observed by optical microscopy and cross-section transmission electron microscopy, only a very small amount of SWNT agglomerates was detected in the black paste. Similar black pastes resulted when the SWNT contents employed were in a range of 3–15 wt%.

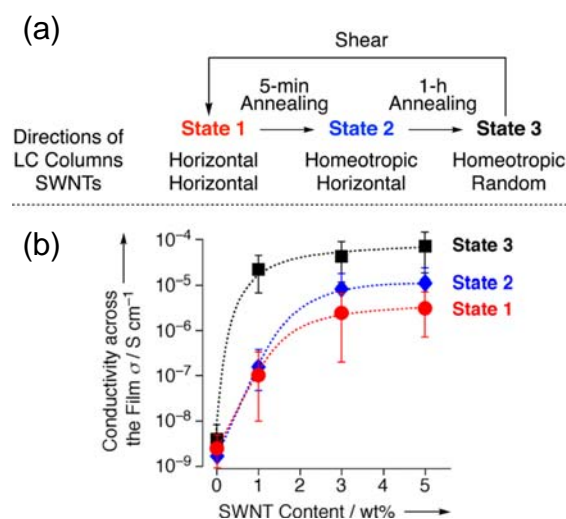


**Figure 1.** a) Molecular structures of TPI<sub>a</sub> and TPI<sub>b</sub>. b) Schematic representations of the LC assemblies with hexagonal columnar and cubic geometries. c) Pictures of a TPI<sub>a</sub>/SWNT composite.

In the course of the above studies, it was serendipitously discovered that the DLC columns of TPI<sub>a</sub>, upon being doped with SWNTs, align homeotropically with respect to the substrate surface. For a clear demonstration of this phenomenon, SWNT-doped TPI<sub>a</sub> was sandwiched by glass plates and allowed to assemble into a LC mesophase by slow cooling (1 °C min<sup>-1</sup>) from its isotropic melt. Polarized optical microscopy (POM) of TPI<sub>a</sub> alone at 25 °C displayed a birefringence texture in the entire view. In contrast, POM of the TPI<sub>a</sub>/SWNT (5 wt%) composite exhibited a dark-field image entirely. Shearing treatment reconfirmed the dark image is attributed to the homeotropic alignment.

During the shear treatment of the TPI/SWNT composites, it was uncovered that SWNTs align along the shearing direction. Polarized absorption spectroscopy of the composite showed that the spectral intensity changes with an applied angle between the polarizing and shear directions. Since SWNT bears a transition dipole along its longer axis, these results clearly indicate that SWNTs in the sheared composite predominantly align along the shear direction.

Of particular interest, the orientation of SWNTs is a dominant factor for charge-carrier transport properties of the TPI<sub>a</sub>/SWNT composite (**Figure 2**). For example, when TPI<sub>a</sub> doped with 1 wt% SWNTs was sandwiched by ITO electrodes, the DC conductivity across the film (s) at 25 °C in State 1 (circles) was nearly two orders of



**Figure 2.** a) Processings and orientational characteristics of States 1–3. TPI<sub>a</sub>/SWNT composites were sheared (**State 1**), shortly annealed for 5 min at 150 °C (**State 2**), and then annealed for 1 h at 150 °C (**State 3**). b) Plots of conductivities across the film (s) of States 1–3 at 25 °C of TPI<sub>a</sub> films doped with 0, 1, 3, and 5 wt% SWNTs, sandwiched by ITO electrodes with a separation of 12.5 μm.

magnitude smaller than that in State 3 (squares). In contrast, State 1 and State 2 (rhomboids) were comparable to one another in DC conductivity, indicating a negligibly small contribution of the LC columns to the observed conduction profile. Similar tendencies have been found in the samples doped 3 or 5 wt% SWNTs.

In summary, imidazolium ion-appended LC TP derivatives are the excellent LC dispersants for pristine SWNTs. Dispersed SWNTs, though randomly oriented in TPI<sub>a</sub>, give rise to a homeotropic orientation of the LC columns up to a macroscopic length scale. Combination of shear and annealing treatments can give rise to three different states in terms of the orientations of the LC columns and SWNTs, where the anisotropy of electrical conduction is determined predominantly by whether SWNTs are oriented or not.

## SECTION □

Homeotropic alignment of DLCs is particularly attracting much attention from researchers because it can maximize anisotropic properties of DLCs along their columns. However, little has been known about the mechanism of the formation of homeotropic alignment. Although many efforts to achieve homeotropic alignment have been made, general strategy has not been established yet. In particular, bilayer homeotropic alignment was remained a great challenge.

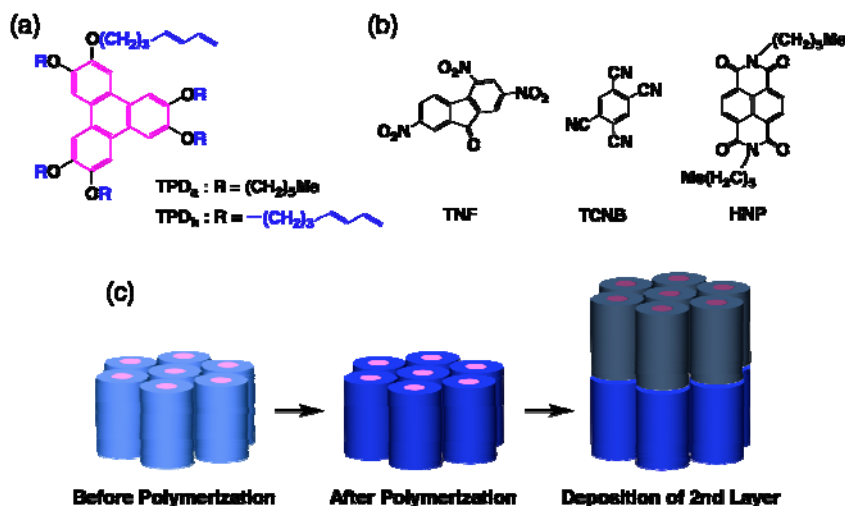
In-situ photopolymerization can be a key breakthrough in this challenge. Kato *et al.* reported that homeotropic alignment could be fixed without structural disturbance even after polymerization. It is expected that polymerized DLCs are chemically and thermally stable enough for the deposition of another layer of DLCs on it. The polymerized homeotropic layer might act as a template for the second layer if both layers have structural similarities. In the section 2, a novel strategy for the formation of homeotropically aligned bilayers are discussed, which is based on the in-situ polymerization of TP-cored DLCs with polymerizable groups.

A spontaneous homeotropic alignment of TP derivatives is relatively reported a lot, especially when modified with certain flexible chains with ether or ester spacers. The polymerizable TP-cored molecule was synthesized by attaching five hexyl and one hept-4,6-dienyl groups to the TP core via ether spacers, where the conjugated diene terminus of the latter works as a polymerizable group (TPD<sub>a</sub>; **Figure 3a**). To form cross-linked network, the monofunctional monomer TPD<sub>a</sub> should be copolymerized with a multifunctional monomer. Therefore, another TP-cored molecule possessing hept-4,6-dienyl groups was also synthesized (TPD<sub>b</sub>; **Figure 3a**). A bilayer homeotropic alignment will be achieved by means of in-situ polymerization as shown in the process in **Figure 3c**. After obtaining homeotropic alignment of DLCs, the alignment will be fixed by polymerization. Then another layer of DLCs will be deposited to achieve bilayer homeotropic alignment.

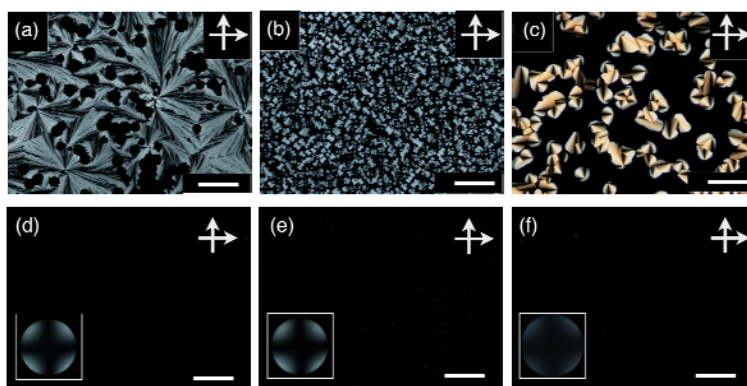
As expected, the mixture of TPD<sub>a</sub> and TPD<sub>b</sub> (with a molar ratio of 17:2; denoted as TPD<sub>c</sub>) showed spontaneous homeotropic alignment during the LC phase on a cooling process (69–33 °C). The in-situ crosslinking of the homeotropically aligned mixture was carried at 55 °C by irradiating UV/visible light under nitrogen gas flow. Through the in-situ crosslinking process, homeotropically aligned hexagonal columnar structure was hardly perturbed, as confirmed by X-ray diffraction analysis and POM. This structural anisotropy was well converted into an electronic anisotropy, confirmed by TRMC. The polymerized homeotropic layer was tolerant of mechanical shearing and the treatment with organic solvents, suitable for the deposition of the second layer on it. Since this thermal and chemical stabilization after the crosslinking, the deposit of another layer on the first layer is allowed.

For the second layer, charge-transfer (CT) complexes of TPD<sub>c</sub> with acceptor molecules were chosen, so that both layers possess similar structures but are of different electrical properties. Three acceptors were employed here, 2,4,7-trinitro-9-fluorenone (TNF), 1,2,4,5-tetracyanobenzene (TCNB) and *N,N'*-(1-hexyl)-1,4,5,8-naphthalenetetracarboxyldiamide (HNP) as shown in **Figure**

**3b.** The CT complexes lost their homeotropic alignment as showing the clear conical textures during POM observation (**Figure 4a, b and c**). However, when they are deposited on the first layer that consists of TP-cored DLCs only, the tendency towards homeotropic alignment was returned (**Figure 4d, e and f**). It is attributed to the inducing effect from the first layer because of similar structures.



**Figure 3.** a) Molecular structures of liquid crystals TPD<sub>a</sub> and TPD<sub>b</sub>. b) Molecular structures of small acceptors of TNF, TCNB and HNP. c) A schematic strategy to achieve bilayer homeotropic alignment. The polymerization of the first layer is precedent to the deposition of the second layer.



**Figure 4.** POM micrographs of CT complex single layers of TPD<sub>c</sub>-TNF (a), TPD<sub>c</sub>-TCNB (b) and TPD<sub>c</sub>-HNP (c) respectively, spun coated on single glass substrates. POM micrographs of double layers consisting of TPD<sub>c</sub>-TNF (d), TPD<sub>c</sub>-TCNB (e) and TPD<sub>c</sub>-HNP (f), deposited on the polymerized TPD<sub>c</sub>. The insets of (d, e and f) are the conoscopic images. Scale bars: 100 μm.