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Highlight

Nanostructured Liquid-Crystalline Semiconductors – A New Approach to Soft Matter Electronics

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In contrast to solid-state organic semiconductors, superstructures can be constructed in liquid-crystalline (LC) phases, using chirality, hybridization with nanofibers, and nanosegregation. Chiral LC molecules form LC phases with helical structures. Gelator molecules self-assemble into fibrous aggregates in LC phases to form nanohybrid materials. Liquid crystal molecules consisting of π -conjugated moieties and incompatible functional parts form nanosegregated LC phases. These nanostructured π -conjugated LC materials have the potential to create new soft matter with unique photonic and electronic functions.

1. Introduction

1.1. Liquid-crystalline semiconductors

In order to fabricate organic electronic devices, homogeneous thin films must be produced by inexpensive processes. Therefore amorphous organic semiconductors including pendant polymers have been used for xerographic photoreceptors^{1a} and electroluminescence devices^{1b} for a long time.¹ The carrier transport processes use charge carrier hopping in energetically disordered systems, described by a Gaussian disorder model^{2a–b} or a small polaron theory.^{2c}

Attempts based on the idea that alignment of π -conjugated chromophores in liquid crystal phases decrease the energetic disorder and increase the effective transfer integral have been executed by a few Japanese researchers.³ However, the current resulting from electronic charge carriers was hidden in the ionic current caused by impurities.^{3a–b} In liquid-crystalline (LC) polymers bearing π -conjugated pendant groups, effective electronic charge carrier transport was not observed because of an insufficient density of chromophores and contamination by impurities.^{3c–d}

In the 1990s, studies of AC conductivity and time-of-flight (TOF) measurements of columnar phases of hexaalkoxytriphenylene derivatives⁴ as well as microwave conductivity measurements of columnar phases of hexabenzocoronene,^{5a–b} phthalocyanine,^{5c–d} and perylene tetracarboxylic bisimide derivatives^{5e} revealed efficient electronic charge carrier transport in the columnar phases. In the smectic phases, electronic charge carrier transport was confirmed for molecules having relatively small π -conjugated chromophores by the TOF technique.⁶ Until now, various liquid crystal molecules including π -conjugated systems associated with electronic charge carrier transport have been synthesized.⁷

These liquid crystals are called LC semiconductors.⁸ Typical LC semiconductors are shown in Fig. 1.

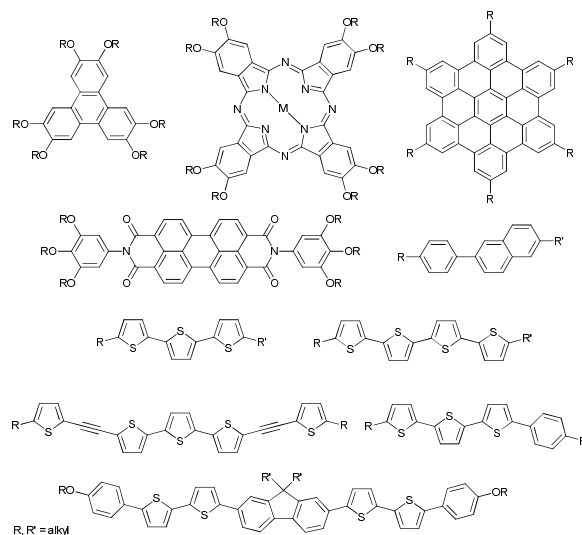


Figure 1 Typical liquid-crystalline semiconductors.

1.2. Applications of liquid-crystalline semiconductors

In this decade, applications of LC semiconductors to electronic devices have been studied. Electroluminescence (EL) devices emitting polarized light were produced using uniaxially aligned photopolymerizable nematic and smectic LC semiconductors.⁹ Field-effect transistors (FET) based on ordered columnar phases and ordered smectic phases were also studied.¹⁰ Extremely high performances were achieved in FETs using polycrystalline thin films of benzothienobenzothiohene derivatives which exhibit ordered smectic phases.^{10e–g} Flexible FETs based on LC thin films on polymer substrates were

produced by the spin-coating method.^{10d} Solar cells using LC hexabenzocoronene and crystalline perylene tetracarboxylic bisimide (PTCBI) derivatives were produced.^{11a} Due to segregation of a PTCBI derivative from a LC component, p-n junctions were spontaneously formed. Solar cells based on LC phthalocyanine derivatives^{11b-c}, LC fluorine derivatives^{11d} and LC diketopyrrolopyrole^{11e} have also been reported.

2. Nanostructured LC electronic systems

Combinations of π -conjugated molecules and superstructures on nanometer scales can produce new electronic and photonic functions. For example, periodical structures on a scale of the wavelength of visible light can interfere with visible light to reflect or confine it and they are called photonic crystals.^{12a} In organic thin film solar cells, the construction of well-defined p-n junctions on a scale of several nm effectively improved their performance.^{12b}

For conventional inorganic semiconductors, micromanipulation is required to introduce periodical superstructures into electronic systems. However, it needs patterning processes that are difficult to apply to mechanically fragile organic systems.

In contrast, self-assemblies of functional molecules can produce periodical structures on various scales in soft matters such as polymers and liquid crystals. Superstructures can be constructed in LC systems by the introduction of chirality,^{13a} photochemical grating,^{13b} and hybridization with nanofibers.^{13c} LC superstructures can also be constructed based on nanophase separation of LC molecules consisting of incompatible parts, as pointed out by Meijer,^{14a} Tschierske,^{14b} and Kato.^{14c-e}

2.1. Construction of hybrid structures based on gel templates

Gelation of liquid crystals has been investigated by Kato and coworkers using molecules bearing hydrogen-bonding sites, which are derived from amino acids.^{14c} The gelator molecules form nanofibrous aggregates through hydrogen bonding in liquid crystals.

Kato *et al.* studied the hybridization of LC semiconductors with hydrogen-bonding gelators. They mixed gelators derived from amino acids with hexaalkoxytriphenylene derivatives, which exhibit columnar phases. Surprisingly, they observed enhanced hole transport in the columnar phases. The hole mobility was increased by a factor of 27 in the case of hexaoxytriphenylene **1** with a gelator **2** derived from L vaniline, as shown in Fig. 2.^{15a-b}

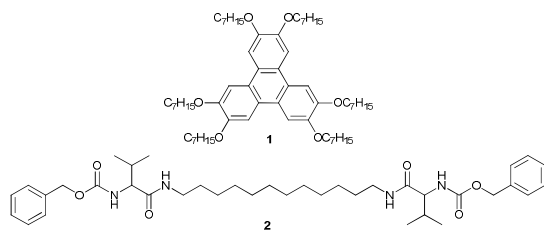


Figure 2 Molecular structures of a hexaalkoxytriphenylene derivative and a gelator derived from amino acids.

Kato *et al.* also designed amide-based gelator molecules bearing π -conjugated moieties as shown in Fig. 3. The gelator **3** bearing tetrathiafulvalene moieties formed uniaxially aligned conductive nanofibrous aggregates in nematic liquid crystals.^{16a} Xerogels consisting of these nanofibers exhibited high conductivity on the order of 10^{-5} Scm^{-1} when they were exposed to iodine vapor. A urea-based gelator **4** bearing phenylbithiophene parts formed uniaxially aligned photoconductive nanofibers under application of an AC electric field in dodecylbenzene.^{16b}

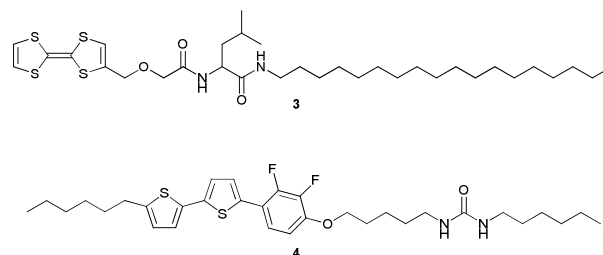


Figure 3 Molecular structures of gelator molecules bearing π -conjugated moieties.

For application to bulk heterojunction solar cells, well-defined nanosegregated structures consisting of p-type and n-type semiconductors should not only increase the efficiency of photocarrier generation but also enhance the carrier transport processes. O'Neill and Kelly constructed a gel network of a p-type LC fluorene derivative penetrated with an n-type PTCBI derivative, as shown in Fig. 4.¹⁷ They coated a mixture of photopolymerizable and non-polymerizable LC dithienylfluorene derivatives **5** and **6** onto a substrate and illuminated UV light on the film to obtain a LC gel thin film. After washing out the non-polymerized component, a layer of n-type PTCBI derivative **7** was deposited on the sponge-like LC film, which had a roughness of several nm. Solar cells were produced using this bilayer film and it exhibited a power conversion efficiency of 0.6 %.

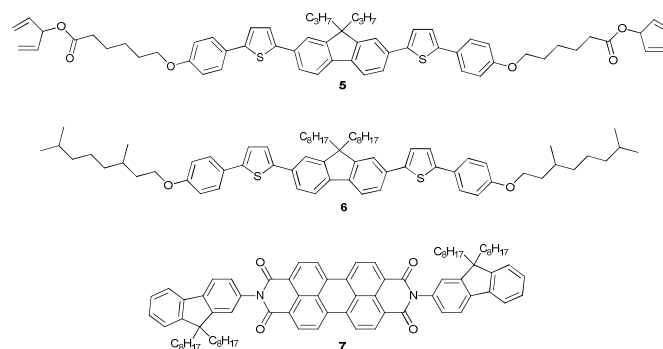


Figure 4 Molecular structures of LC semiconductors used to form gel networks.

2.2. Construction of periodical structures in LC π -conjugated systems for photonic functions

Combination of electroluminescence devices with photonic structures can enhance light emission. Kitzerow *et al.* fabricated

electroluminescence devices using the electron transporting LC perylene tetracarboxylate **8** and a hole transporting triphenylamine derivative **9** on microresonators with a multilayer structure of dielectrics (Fig. 5).¹⁸ Enhanced EL spectra with narrow widths were observed for the devices.

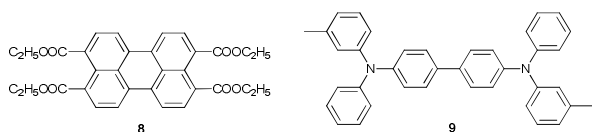


Figure 5 Molecular structures of the organic semiconductors used for the EL devices with microresonators.

A cholesteric phase has a helical structure with a periodicity on the scale of the wavelength of visible light, and it reflects or confines the visible light. Records of images^{13a} and laser emission¹⁹ in the cholesteric phases have been studied. Another characteristic of cholesteric LC is to transmit circularly polarized light with the same helicity as the cholesteric LC and to reflect light with a reversed sign. However, most cholesteric liquid crystals are electronically inactive.

Cholesteric liquid crystals bearing a π -conjugated moiety have been reported (Fig. 6).²⁰ O'Neill and Kelly reported that the cholesteric LC **10** based on bithienylfluorene bearing chiral alkyl chains emitted circularly polarized light by the excitation of UV light.^{20a} The width of its reflection band reached 200 nm due to its large birefringence, and the dichroic ratio exceeded 10 within the reflection band. Funahashi and Tamaoki synthesized the cholesteric LCs **11a–b** bearing quaterthiophene moieties and a chiral binaphthyl part. These exhibited a cholesteric phase at room temperature and emitted circularly polarized fluorescence.^{20b}

In contrast to the smectic and columnar phases in which efficient electronic carrier transport is possible due to large intermolecular π -orbital overlap, only ionic conduction had been observed for a long time. However, hole transport was recently confirmed in the nematic and cholesteric phases of liquid crystals bearing large π -conjugated cores.^{20c–e}

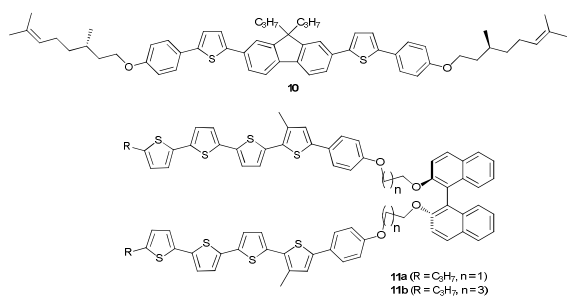


Figure 6 Molecular structures of LC semiconductors exhibiting selective reflection.

Photochemical reactions can produce photonic structures with periodicities on the scale of the wavelength of visible light. O'Neill and Kelly constructed periodical structures in films of photopolymerizable LC semiconductor **12** using a surface relief grating method, as shown in Fig. 7. They observed an

enhancement of the photovoltaic effect in bilayer solar cells comprised of a grating LC hole transport layer and an electron transport layer of compound **7**.²¹

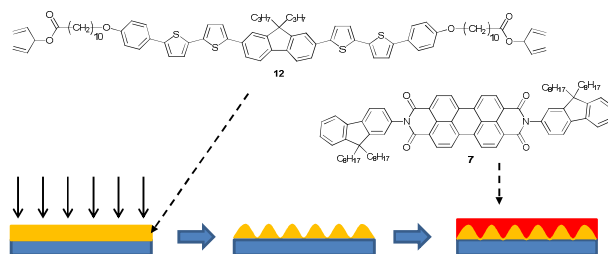


Figure 7 Schematic image of a superstructure produced in LC systems by a surface relief grating method.

2.3. Construction of superstructures through nanosegregation

Amphiphilic molecules have a tendency to form supramolecular self-assemblies such as nanofibers, nanotubes, and nanocapsules. In particular, supramolecular self-assemblies consisting of amphiphilic π -conjugated molecules have been extensively studied by Würthner,^{22a–c} Aida,^{22d–e} Ajayaghosh,^{22f–g} Meijer,^{22h} Schenning,²²ⁱ and Müllen.^{22j}

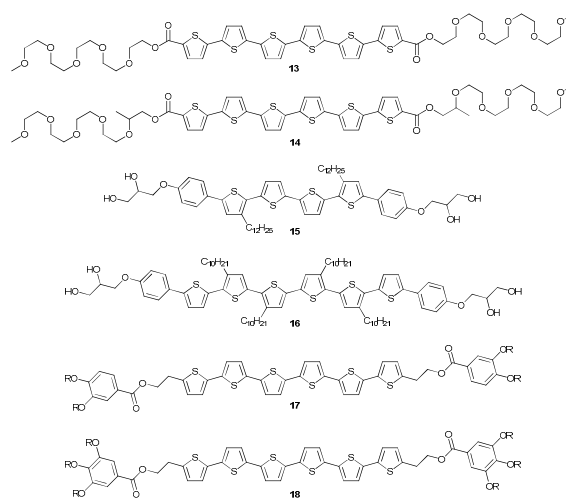


Figure 8 Oligothiophene derivatives exhibiting nanosegregated LC phases.

For LC systems, the molecules consisting of π -conjugated parts and their incompatible moieties (Fig. 8) form nanosegregated LC phases. Meijer *et al.* synthesized sexithiophene derivatives **13–14** bearing oligoethylene oxide chains.^{23a} These compounds exhibited smectic phases in which rod-like rigid π -conjugated parts and flexible oligoethylene oxide chains formed separately assembling coils. Tschierske *et al.* constructed honeycomb-like network structures of hexagonal and square cylinders using oligothiophene compounds **15–16** bearing hydrogen-bonding glycerol groups as well as hydrophobic lateral alkyl chains.^{23b–c}

Yasuda and Kato synthesized polycatenar LC molecules **17–18** consisting of four or six alkyl chains and an oligothiophene moiety.^{23d} Because of the competition of π - π interaction between the π -conjugated cores with van der Waals

interaction between alkyl chains, nanosegregated LC phases which had layered, columnar, and micellar cubic structures were formed. The hole mobility determined by the TOF method increased to the order of $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in the columnar phases, while efficient hole transport was not observed in the micellar cubic phases.

Nanosegregated LC phases are also formed by molecules with π -conjugated and ionic moieties. These nanosegregated structures can be expected to be mixed conductors that can transport ions as well as electronic charge carriers. The combination of electronic functions with ionic transport can create new optoelectronic devices.²⁴

Figure 9 shows ionic π -conjugated LC molecules. Aida and Fukushima synthesized a hexaalkoxytriphenylene derivative **19** bearing imidazolium moieties at the ends of the alkyl chains.^{25a} This compound exhibited a columnar phase and can be hybridized with ionic liquids^{25a} as well as carbon nanotubes.^{25b} Müllen *et al.* also reported that hexabenzocoronene derivatives **20** bearing imidazolium moieties formed nanofibers in the solution state as well as columnar organization in their solid states. In the solid state, aromatic and ionic parts assembled separately.^{25c}

Funahashi and Kato synthesized phenylterthiophene derivatives **21–23** bearing imidazolium groups which exhibited nanostructured smectic phases.^{26a–b} The competition of strong electrostatic interaction between the ionic parts with the π - π interaction resulted in the formation of layer structures where sheets consisting of π -conjugated moieties were separated by a two-dimensional mantle formed by ionic parts. In the smectic phases of the compounds, electronic charge carriers are transported within the sheets made from π -conjugated cores and ions can move within the two-dimensional mantles. It should be noted that the liquid crystals exhibit electrochromism under the application of DC bias without electrolyte solutions.

In 1986, the first redox-active LC viologen derivative was reported by Tabushi *et al.*^{27a} Chang and Kitagawa have studied a redox-active LC bipyridine platinum complex **24** that exhibits a hexagonal columnar phase.^{27b} Its spin-coated film exhibited reversible electrochromism in an electrolyte solution.

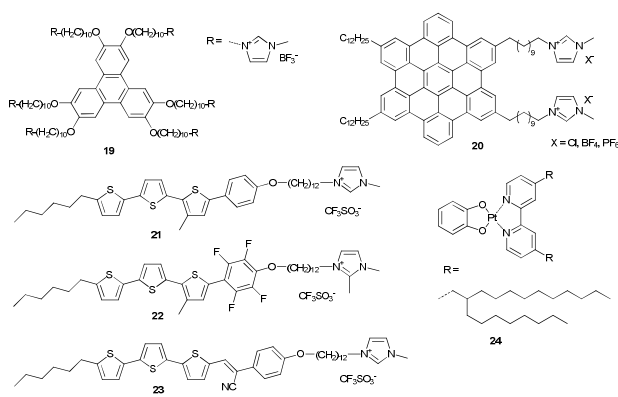


Figure 9 Molecular structures of π -conjugated LC molecules bearing ionic moieties.

Modification of LC molecular aggregation by hydrogen bonding has been studied by Kato *et al.*^{14c} Nanofibrous supramolecular aggregates bearing hydrogen bonding sites and π -conjugated moieties have also been studied.^{22g}

Yagai *et al.* synthesized a PTCBI derivative **25** bearing a hydrogen-bonding cyanurate part as shown in Fig. 10.²⁸ A mixture of this compound **25** and a melamine derivative **26** formed a thermoresponsive supramolecular aggregate. Above 150 °C, the mixture exhibited a hexagonal columnar phase while lamellar organization was observed below 150 °C. Microwave absorption measurements revealed electron mobilities on the order of $10^{-1} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ in the LC phases.

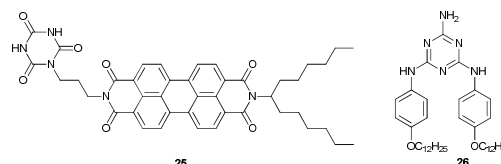


Figure 10 Molecular structures of a PTCBI derivative bearing a hydrogen bonding site and a melamine derivative.

2.4. Nanosegregated LC p-n junctions

For improvement in the performance of bulk heterojunction organic solar cells, well-defined nanosegregated structures on a scale of several tens of nanometers are required because the scale is comparable to the diffusion length of excitons.^{12b} Moreover, a closed molecular aggregation and small energetic disorder in the LC phases can also enhance carrier transport.

The incorporation of p-type and n-type segments in a single molecule should be effective in forming p-n junctions on a nanometer scale because of nanosegregation between the two segments. Figure 11 shows LC molecules consisting of p-type and n-type moieties. Pisula and Müllen reported columnar LCs **27** in which n-type PTCBI moieties are located radially around p-type hexabenzocoronene cores.^{29a} The LCs form a core-shell structure in which an electron-donating one-dimensional core is surrounded by an electron-accepting shell mantle. Yasuda and Kato reported LC molecules **28** in which an electron-accepting core is surrounded by electron-donating moieties. Ambipolar charge carrier transport was observed in the columnar phase.^{29b} Yasuda and Adachi also reported LC semiconductors **29** consisting of electron-donor and -acceptor parts and applied them to bulk heterojunction organic solar cells.^{29c}

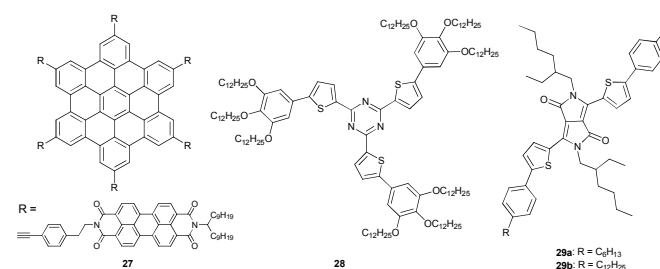


Figure 11 Molecular structures of LC semiconductors consisting of electron-donor and acceptor moieties.

Fullerene derivatives are typical n-type semiconductors. Figure 12(a) exhibits LC molecules consisting of a fullerene moiety and p-type π -conjugated parts. Deschenaux *et al.* synthesized LC fullerene derivatives **30** bearing an electron-donating oligophenylene vinylene moiety. In the LC phases, bilayer structures were formed and the fullerene parts were segregated between the layers consisting of dendritic mesogenic moieties.^{30a} Imahori *et al.* reported a LC dyad **31** consisting of fullerene and phthalocyanine parts. The dyads exhibited a columnar phase; phthalocyanine cores stack to form one-dimensional columnar aggregates, around which fullerene moieties coiled themselves, as shown in Fig. 12 (b).^{30b} TOF and microwave absorption measurements indicated efficient hole and electron transport in the columnar phases. Hole transport proceeds through the columnar aggregates of phthalocyanine cores while electron transfer occurs between the fullerene moieties. The same dyads were also reported by Ohta *et al.*^{30c}

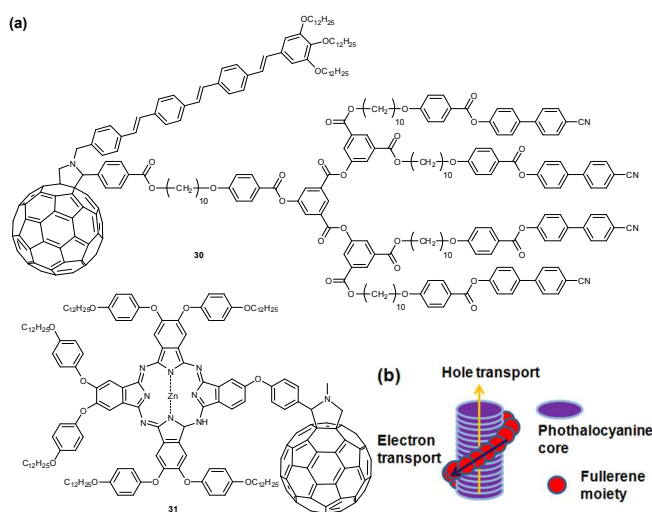


Figure 12 (a) Molecular structures of LC molecules consisting of phthalocyanine and fullerene moieties. (b) Schematic of ambipolar carrier transport in the columnar phase of compound **31**.

LC block copolymers consisting of p-type and n-type segments also exhibit a nanosegregated LC phase (Fig. 13). Thelakkat *et al.* synthesized LC block copolymer **32** consisting of a poly(3-alkylthiophene) block and a polyacrylate segment bearing PTCBI parts in the side chains.^{31a} Geng *et al.* reported π -conjugated oligo(dithienofluorene) **33** bearing a PTCBI part and solar cells based on the π -conjugated oligomer, which exhibited a power conversion efficiency of 1.5%.^{31b}

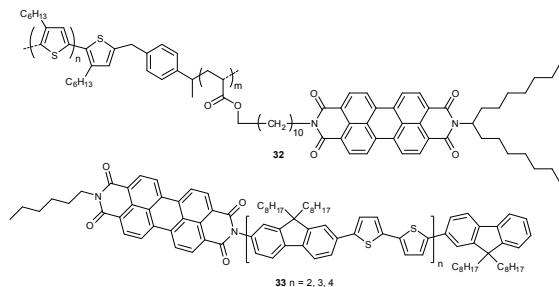


Figure 13 LC conjugated polymers consisting of electron-donor and acceptor segments.

Bent-core liquid crystals exhibit ferroelectric LC phases and have been extensively studied.^{32a} Recently Walba *et al.* have found helical nanofilament phases consisting of bent-core liquid crystal molecules (Fig. 14).^{32b} They prepared composites consisting of compound **34** and fullerene derivatives and observed more enhanced photocarrier generation and transport in the helical nanofilament phase than in the lamellar LC phase.^{32c}

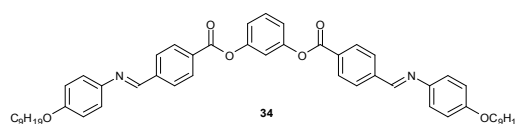
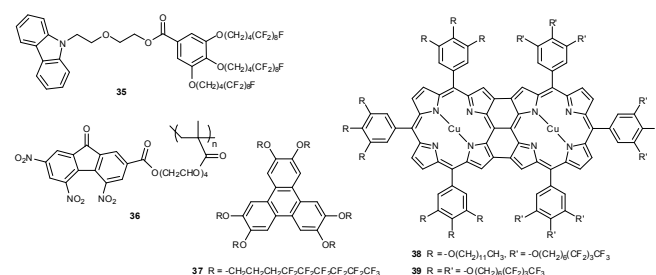


Figure 14 Molecular structure of a bent-core liquid crystal **34** exhibiting a helical nanofilament phase

2.5. Nanostructured LC phases by segregation of side chains

In general, liquid crystal molecules consist of aromatic cores and alkyl chains. In the classical description, LC phases appear as a result of strong interaction between the π -conjugated cores moderately weakened by thermal motion of the alkyl chains. Yoneya pointed out the significance of nanosegregation between the aromatic cores and alkyl chains in the formation of LC phases.³³ Therefore, incompatible side chains with aromatic cores instead of alkyl chains can induce mesophases.

Perfluoroalkyl groups promote nanosegregation in LC systems because of strong interaction between them. Figure 15 shows examples of π -conjugated LC molecules bearing perfluoroalkyl chains. Percec and coworkers prepared columnar LC complex consisting of an electron-donating compound **35** bearing perfluoroalkyl chains and an electron-accepting pendant polymer **36**.^{34a} Shimizu *et al.* synthesized a LC triphenylene derivative **37** bearing perfluoroalkyl chains.^{34b} The compound exhibited a nanosegregated columnar phase because of strong interaction between perfluoroalkyl chains. Aida and co-workers synthesized a fused metalloporphyrin dimer bearing 18 semifluoroalkyl groups and a dimer bearing 9 semifluoroalkyl chains as well as 9 alkyl moieties.^{34c} In spite of having the same structure of its aromatic parts, compound **38** exhibited a rectangular columnar phase in contrast to the orthorhombic columnar phase of compound **39**. Surprisingly, electron transport was observed in the rectangular columnar phase of compound **38**, while hole transport was dominant in the orthorhombic columnar phase of compound **39**.



37 R = -O(CH₂)₁₁CH₃, R' = -O(CH₂)₆(CF₂)₃CF₃
38 R = R' = -O(CH₂)₆(CF₂)₃CF₃
39 R = R' = -O(CH₂)₆(CF₂)₃CF₃

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Figure 15 Molecular structures of discotic liquid crystals bearing perfluoroalkyl groups.

In electronic device applications, extended π -conjugated systems are indispensable for the enhancement of carrier transport and visible light absorption. However, the extension of π -conjugated systems lowers the solubility of the materials and promotes their crystallization. Branched alkyl chains are effective for inhibiting the aggregation of the extended aromatic moieties, although carrier transport is also degraded by the decrease of intermolecular orbital overlaps and the increase of structural disorder.³⁵

Gregg *et al.* synthesized LC PTCBI derivatives **40–42** bearing hydrophilic oligoethylene oxide chains, as shown in Fig. 16.^{36a–b} They exhibited LC phases having lamellar structures over wider temperature ranges while hexa- or tetra-alkylated PTCBI derivatives exhibited columnar phases in the high temperature region, as reported by Würthner *et al.*^{7a–b} Moreover, they synthesized LC PTCBI derivative **42** bearing an ammonium group at the terminal of the side chain.^{36c–d} The compound can be doped with metallic Na in THF solution; the perylene core is reduced by Na, producing an anion radical species, which is stabilized by the ammonium cation on the side chain. Increasing the dopant concentration by over two orders enhanced the conductivity of the doped thin film of the compound by over four orders of magnitude.

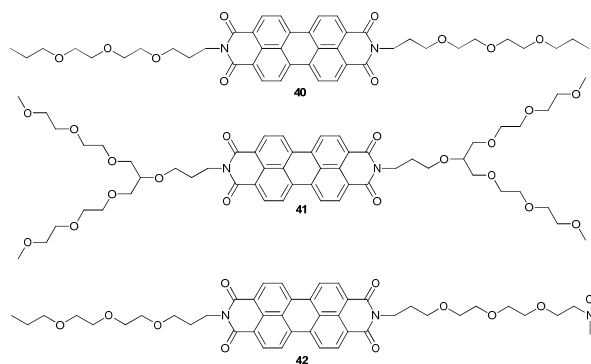


Figure 16 Molecular structures of PTCBI derivatives bearing oligoethylene oxide chains.

LC oligomers based on silsesquioxane cores appended to mesogenic units were first reported by Mehl and Goodby.^{37a} Liquid crystals bearing disiloxane and trisiloxane chains have been studied, and the stabilization of the smectic layer structures due to nanosegregation between the flexible oligosiloxane units and aromatic cores has been reported.^{37b–e}

Guillon *et al.* synthesized LC triphenylene derivatives bearing oligosiloxane chains.^{37f} They exhibited columnar phases, but electronic properties were not reported. Funahashi *et al.* synthesized PTCBI derivatives bearing oligosiloxane chains, as shown in Fig. 17.^{38a–b} Compound **43** exhibited columnar phases at room temperature and it did not crystallize even when it was cooled to -100 °C. Moreover, they are soluble in various organic solvents and their thin films can be produced by a spin-coating method. The electron mobilities of the LC

PTCBI derivatives were determined by a time-of-flight technique. In the ordered columnar phase of compound **43**, the electron mobility exceeded $0.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ at room temperature.^{38b} The electron transport mechanism in the columnar phases is described by a Gaussian disorder model.^{38c}

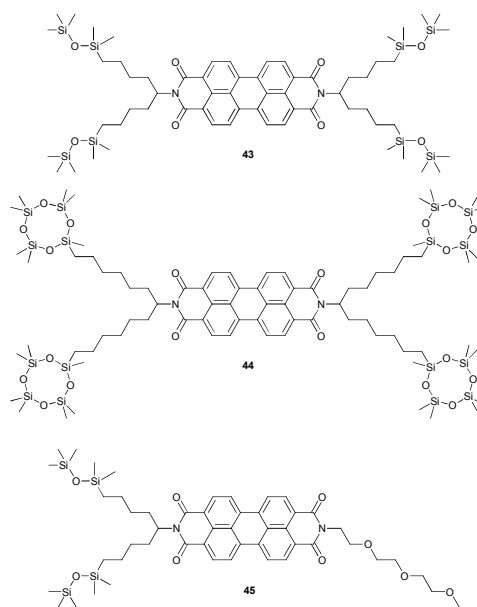


Figure 17 Molecular structures of LC PTCBI derivatives bearing oligosiloxane moieties.

Funahashi and co-workers synthesized LC PTCBI derivative **44** bearing cyclotetrasiloxane rings.^{38d} This LC compound also exhibited a columnar phase at room temperature and it did not crystallize on cooling to -100 °C. Nanosegregation between the aromatic cores and cyclotetrasiloxane rings was significant in the formation of the columnar phase. In the columnar phases of the PTCBI derivatives bearing oligosiloxane moieties, a kind of core-shell structure in which crystal-like one-dimensional aggregates of π -conjugated cores were surrounded by flexible shells consisting of oligosiloxane moieties were formed by the nanosegregation. Asymmetric PTCBI derivative **45**, bearing triethylene oxide chains, exhibited a lamellar organization instead of a columnar structure.^{38e}

Conclusions

The formation of dynamic and flexible nanostructures that enhance photonic and electronic properties are one of the characteristic features of LC systems. Through their nanostructures, various physical and chemical properties can be coupled to produce new functions in LC systems, unlike conventional crystalline and amorphous semiconductors. Combinations of electro-active π -conjugated systems and periodical structures based on chirality can create photonic semiconductors. Hybridization of gel networks and LC systems or nanosegregation between p-type and n-type segments in LC molecules should produce efficient p-n junctions at high

densities. Competition between ionic and π - π interactions forms nanostructured soft systems with electronic functions. Side chains other than alkyl groups promote nanosegregation and realize new LC electronic materials.

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