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By

Bin Wang

A dissertation submitted to the Graduate Faculty in Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy

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This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

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Abstract


By

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Organic semiconducting materials have been under intensive investigation in the recent decades for potential applications in various electronic or optoelectronic devices such as light emitting diodes, photovoltaic cells and field effect transistors. Compared to inorganic counterparts, organic charge transport materials are attractive for their abilities of forming thin-films, large area manufacturing, compatibility with flexible substrate, light weight and potential low fabrication cost. The charge transport property of the organic active layer is one of the key factors to the electronic or optoelectronic performance of devices. Research projects presented in this thesis focused on improving charge carrier mobility of organic charge transport materials as it is a property determined by the hierarchical structure of the material. Strong effort has been made to the design of advanced molecular structures and controlling self-assembly behaviors. Chapter 1 introduces the general background of charge transport materials, including: the nature of charge transport in organic semiconducting materials, three widely used methods for charge carrier mobility measurements and the current development of organic charge transport materials. Advantages and drawbacks in applications were analyzed with ordered and disordered organic systems. A more thorough review was given to the engineering and the application of the discotic columnar liquid crystalline (DCLC) phase. Chapter 2 describes a DCLC phase with a novel hierarchical structure in which each supra-molecular column features a bundled-stack
structure. The molecular design rationale was explained and the thermal behavior and phase structure were characterized. Charge carrier mobility of compound 1 was measured to be 0.05 cm²V⁻¹s⁻¹ with pulse radiolysis time-resolved microwave conductivity. The incorporation of the bundled stack structure may potentially be a fundamental solution towards enhancing the organic semiconductor’s electronic performance. Chapter 3 introduces three chain functionalized perylene tetracarboxylic monoimide diester derivatives (PEIs) with monotropic DCLC phases. The intra-column rotation angle was determined to be 60° between neighboring PEI molecules, which is a substantial improvement of the transfer integral compared to the perylene tetracarboxylic diimides with a 90° rotation angle. The rotation angle was further tuned by incorporating branched aliphatic substitution to the PEI core as described in chapter 4. By reducing the length of the alkyl swallow tail, the rotation angle changes from 60° to 72° which is even more favorable to the electronic coupling between neighboring PEI units. Through those studies, we have shown that the engineering of DCLC phase may lead to substantial improvements on charge transport properties of organic semiconducting materials.
In memory of my grandma

and

dedicated to my beloved family
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CHAPTER 1. INTRODUCTION

1.1. Conductivity and charge carrier mobility

Electrical current is the flow of charge carriers which could be electrons, holes or ions depending on the type of conductive materials. For most of metals, their outer shell electrons are delocalized and free to move. Under external electric field, the moving of electrons results in a net flow of negative charges. The electrical conductivity $\sigma$ describes the ability of the material to conduct electrical current and is measured with the ratio of the current to the applied electric field.

$$I = \sigma \cdot E$$

Metals or other conductors have large $\sigma$ values that are usually close to or higher than $10^6$ S/m. Insulators, on the other hand, are typically below $10^{-8}$ S/m. From the conductivity point of view, materials that have $\sigma$ values in between two extremes are considered to be semi-conductors. Electrons in semiconductors are bounded quite strongly that without excitation it is difficult to conduct charges. Quantum mechanics tells us that energies of electrons in one atom are not continuous. There are energy levels that are allowed for electrons to occupy while others are forbidden. When allowed energy states are both energetically and spatially close together, band structure forms as the combination of those energy states. Two energy bands are particularly important when conductivity of a semiconductor is discussed: the valence band in which electrons are at their ground states, and the conduction band in which electrons have higher energies but are able to be delocalized. The gap in between is called the forbidden band or band gap where electrons with such energy levels are impossible to exist. According to the band theory, electrons jumping to the conduction band as the result of energy input become free charge carriers which result into electrical current under the influence of external electric field. At the
same time, the vacancies left in the valence band are driven to the opposite direction and serve as free carriers of another type. Energies required for such excitation can come from heat, light or in a different way, from doping. Comparing to typical metal conductors, the different mechanism of charge conduction gives rise to various properties that are unique to semiconducting materials.

Regardless of the type of materials, electrical conductivity is generally affected by two crucial factors: 1. how many free carriers are moving; 2. how fast charge carriers move in an electric field. For any given material, the first factor can be reflected by free carrier concentration. The latter is characterized by charge carrier mobility $\mu$, which is defined in the equation below with the unit of cm$^2$/V$\cdot$s ($v_d$ is the carrier drift velocity):

$$v_d = \mu \cdot E$$

Therefore, the relationship of carrier mobility with conductivity can be described as:

$$\sigma = n \cdot e \cdot \mu$$

Compared to the inorganic counterparts, organic charge transport materials are attractive for their abilities of forming thin-films, large area manufacturing, compatibility with flexible substrate, light weight and potential low cost. Applications have been found with field effect transistors (FET), photovoltaic (PV) devices and light emitting diodes (LED), etc.

Typical metal conductors could be viewed as the collection of positive metal ions emerged in the “sea” of free electrons. The free moving charge is so abundant that it posts no limitation on the material’s conductivity. Electrical resistance can be attributed to defects in the crystal lattice along with the scattering of electrons caused by thermal motion of atoms. Therefore, conductors’ conductivity decreases as temperature increases. In contrast, a semiconductor has band structure and electrons are much more localized. Since electrons in
fully occupied bands are not mobile, only excited conduction band electrons and valence holes contribute to the total carrier concentration. A typical inorganic intrinsic semiconductor such as silicon has a carrier concentration of $10^{10}$ cm$^{-3}$ at room temperature (RT) due to thermal excitation. Therefore, semiconductors’ conductivity increases as temperature becomes higher. Compared to the inorganic counterparts, organic semiconductors have extremely low intrinsic carrier concentration, merely ca. 1 cm$^{-3}$ for most aromatic compounds. This is because of the much wider energy band gap and low dielectric constant, which makes it very difficult to excite valence electrons and separate excitons. In reality, it is hard to obtain extremely pure organic compounds. Charge carriers contributed by impurities lead to actual carrier concentrations much higher than 1 cm$^{-3}$.

Even an impure organic compound’s conductivity suffers from low charge carrier concentration. However, the charge drifting rates in those compounds can be high when certain conditions are satisfied. That is to say, provided with enough carrier concentration, organic compounds are potentially capable of achieving high conductivities which makes design and fabrication of high performance electronic and optoelectronic devices possible. While doping, photo-excitation, or charge injection from electrodes could efficiently increase carrier concentration by orders of magnitude, carrier mobility is a property more intrinsic of the material itself, which is eventually decided by its hierarchical structure. Therefore, improving charge carrier mobility by designing advanced molecular structures and controlling self-assembly behaviors has become the center of exploring and inventing novel high performance organic charge transport materials.

There are a handful of methods being employed by material scientists to determine the carrier mobility of a material such as time of flight (TOF), steady state trap free space charge
limited current (TF-SCLC), dark injection space charge limited current (DI-SCLC), pulse radiolysis time-resolved microwave conductivity (PR-TRMC), conductivity measurement of OFETs, and measurement of transient electroluminescence (Transient EL).

Hereby, we briefly explain three most commonly used methods: TOF, TF-SCLC and PR-TRMC. TOF method measures the carrier drift velocity directly. Experimental set-up is illustrated below in Figure 1.1.1. The electrode on the top is semitransparent to visible light. Both electrodes are selected to be unable to inject electrons or holes into the sample. During a measurement, a pulse of laser is sent to the top of the sample generating excitons. With an externally applied electric field, excitons separated into charges and drift in a sheet towards two electrodes. The pulse of laser is set to be much shorter than the transit time (time required for carriers to move from one electrode to the other). Moreover, the laser pulse is strongly absorbed by only a small fraction of sample near the transparent electrode which is much thinner compared to the total thickness. The time-dependent electric current is recorded by an oscilloscope. An analysis of data yields the drift velocity and charge carrier mobility of the material.

![Figure 1.1.1. Experimental set-up of TOF measurement](image-url)
TF-SCLC measurements can be done with much more economical and simpler equipment. Comparing with TOF, it does not require an oscilloscope, or a pulsed laser. Charges are directly injected from an electrode, followed by drifting across the sample. The steady current is measured against the swept voltage. It is imperative that the electrode responsible for charge injection forms an ohmic contact with the tested sample so that the contact resistance is much smaller than the sample resistance. During measurement, the applied electric field is adjusted to be large enough so that the current is bulk limited (space charge limited). I-V curve is then analyzed to solve the carrier mobility.

Results obtained from both TOF and TF-SCLC methods are greatly influenced by the molecular alignment in the device. For example, the molecular alignment and domain size of LC material could lead to profound differences in experimental mobility values that may vary in several orders of magnitude. Measures such as sealing device with adhesives or taking measurement under an inert environment may also be desired in order to avoid mechanical interferences as well as chemical interferences from atmosphere.

PR-TRMC is a contact free measurement. A pulse of highly energized electrons is sent to the sample to provide the energy needed for the formation of charge carriers. As the result, the conductivity of the sample increases since the carrier concentration increases. This change could be calculated from the change of microwave power reflected by the tested sample. The frequency of microwave controls the time that carriers could drift along one direction and thus controls the locality of the conductivity measurement (usually a few nanometers). Therefore, PR-TRMC does not provide information reflecting the device performance. Instead, it provides the upper limit of a sample’s carrier mobility.

TOF method is more commonly used compared to TF-SCLC because forming ohmic
contact at the interface between electrodes and organic charge transport layer could be challenging. The energy difference between LUMO of sample and the Fermi level of the cathode is considered to be the energy barrier that hinders the electron injection. Usually, for hole injection, the contact behaves as an ohmic one when this energy barrier is smaller than 0.3 eV. There are mainly three ways to obtain an ohmic contact: 1. Select electrodes with a proper work function so that the energy barrier could be lowered; 2. Dope the organic charge transport layer so that the demand for charge carriers through external charge injection will be decreased; 3. Increase the thickness of the organic charge transport layer so that the resistance at contact would become smaller part of the total device resistance. Evidences have shown to support those ideas as they either help improving the carrier concentration needed to achieve space charge limited current, or decreasing the magnitude of the space charge limited current so that the need for the carrier concentration is suppressed. In reality, it is sometimes not easy to judge if the contact is ohmic and the current is space charge limited. For this reason, TOF and PR-TRMC are considered to be more reliable carrier mobility measurements.

As mentioned above, organic charge transport materials are semiconductors when free carriers concentration is not intrinsically limited. On the other hand, charge carrier mobilities are dependent on the hierarchical structure of the material, electric field, temperature or the nature of the carriers. Carrier mobilities for organic semiconductors are in the range of very low (e.g., $10^{-7}$ cm$^2$V$^{-1}$s$^{-1}$ for poly(N-vinylcarbazole)) to as high as intrinsic inorganic semiconductors (Intrinsic Si mobilities: 1350 cm$^2$V$^{-1}$s$^{-1}$ and 480 cm$^2$V$^{-1}$s$^{-1}$ for electron and hole transport, respectively).

As designers, we are particularly interested in problems and phenomena related to the material hierarchical structure. There are generally two factors in balance that determines how desirable a material is in applications: performance and cost. Single crystals usually exhibit
highest carrier mobilities due to their exceptional long-range order that leads to enhanced electronic wave function coupling and well defined molecular orientation. As determined by the TOF method, mobility values of 1.7 cm$^2$V$^{-1}$s$^{-1}$ and 0.5 cm$^2$V$^{-1}$s$^{-1}$ for holes and electrons respectively have been found with single crystal C$_{60}$.\textsuperscript{9} Approximately 1 cm$^2$V$^{-1}$s$^{-1}$ was reported for anthracene materials.\textsuperscript{10} Single crystalline rubrene has been widely investigated as p-type semiconducting active material in FETs and was reported to exhibit hole mobilities up to ca. 40 cm$^2$V$^{-1}$s$^{-1}$ at room temperature.\textsuperscript{11} However, large-scale growth of single crystals on a device substrate is difficult and expensive to industrial manufacturing. Therefore, polycrystalline materials have been introduced as an alternative for their cost-friendly film-forming ability. Mostly used in OFETs and OLEDs, the electronic performance of the polycrystalline material is limited by the grain size, grain boundaries and the molecular orientation.\textsuperscript{12} Polycrystalline materials, such as di(2-thienyl)naphthodithiophene, dithienylanthracene, di-substituted oligothiophenes, and pentacene, etc., are showing mobilities in the range of ca. 10$^{-4}$ to 1 cm$^2$V$^{-1}$s$^{-1}$.\textsuperscript{13} Obviously, this money-saving approach comes at the price of poorer performance.

Amorphous material has advantages such as easy fabrication, flexibility and transparency. However this class of material is generally characterized by the lowest carrier mobilities among all three morphologies. Most of devices based on an amorphous active component have shown mobility values in the range of 10$^{-6}$ to 10$^{-2}$ cm$^2$V$^{-1}$s$^{-1}$.\textsuperscript{14} In general, relatively high carrier mobilities were found with hole-transporting amorphous materials, such as thiophene- and selenophene-containing tris(oligoarylenyl)amines, showing a value in the order of 10$^{-2}$ cm$^2$V$^{-1}$s$^{-1}$. In contrast, most of n-type amorphous materials display mobilities that are below the level of 10$^{-3}$ cm$^2$V$^{-1}$s$^{-1}$ (e.g., 2×10$^{-4}$ cm$^2$V$^{-1}$s$^{-1}$ for 2,5-bis(6-(2,2'-bipyridyl))-1,1-dimethyl-3,4-diphenylsilole). However, some of n-type amorphous materials are exceptions as their mobilities are in
the range of $10^{-3} \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. 

![Image of molecular structures](image)

**di(2-thienyl)naphthodithiophene**

**di-thienylanthracene**

**di-substituted oligothiophenes**

**pentacene**

**di-substituted oligothiophenes**

**Figure 1.1.2.** Molecular structure of charge transport polycrystalline materials
Figure 1.1.3. Molecular structure of charge transport amorphous materials

2,5-bis(6'-2',2''-bipyridyl))-1,1-dimethyl-3,4-diphenyl silole

thiophene- and selenophene-containing tris(oligoarylenyl)amines

Figure 1.1.4. Molecular structures of charge transport single crystalline materials

Anthracene

Naphthalene

Rubrene

Perylene
Generally, hole-transporting (or p-type) materials are under wider and more extensive study than electron-transporting (or n-type) materials. It is also important to note that hole-mobilities are often 1 or 2 orders of magnitude higher than electron-mobilities found with the same or similar materials. Purity is another important factor which tremendously affects the actual electronic performance. Impurities act as traps that temporarily or even permanently hold free carriers from continuously hopping. Studies have shown that by taking measures to further purify organic materials beyond synthetic level (ultrapure), organic single crystals exhibit very high electron or hole mobilities. The ultrapure naphthalene single crystal has a hole mobility of ca. 400 cm$^2$V$^{-1}$s$^{-1}$, while electron mobility of ca. 100 cm$^2$V$^{-1}$s$^{-1}$ has been reported for ultrapure perylene single crystals as measured by the TOF method.$^{16}$

1.2. Liquid crystalline phases and their applications in electronics

Combining order and molecular mobility, liquid crystalline (LC) materials have become promising candidates for applications in charge transport. Materials exhibit a LC phase are able to provide carrier mobilities comparable to those of polycrystalline materials and in some cases approaching those of single crystals while preserving the low cost and facile fabrication which is usually associated with amorphous materials.$^{17}$ Properties such as self-healing, self-organization and the ability to respond to external stimuli are also favored by some applications.

First liquid crystals were discovered in late 19$^{th}$ century with cholesterol derivatives. Those compounds exhibit two “melting points”. As temperature increases above the first “melting point”, the compound begins to acquire fluidity which clearly belongs to a conventional liquid. At the same time, its anisotropic property remains as that of crystals. Keep increasing temperature will bring the compound to a completely molten state in which it behaves in every
way as a conventional isotropic liquid. The phase between two “melting points” is referred as a mesophase. It was later understood through structural analysis that those compounds in a mesophase combine flexibility and order at both the microscopic and the macroscopic level.

There are thermotropic and lyotropic liquid crystals which are classified based on the dependence of different external condition changes. The appearing of a mesophase of a thermotropic liquid crystal is closely related to the change of temperatures, while lyotropic liquid crystals exhibit a mesophase when certain solution conditions such as concentrations are satisfied. In this thesis, we focus on the thermotropic liquid crystals as essentially all electronic applications only involve neat compounds in their condensed states.

According to the degree of order, liquid crystalline materials can be classified into mainly four types: nematic, smectic, cubic and columnar mesophases. In a nematic system, molecules are arranged with only long-range molecular orientational order. In the rest of three phases, however, both molecular orientational and positional long-range order could be found. Smectic phases are usually characterized by a lamellar structure in which molecules arrange themselves into two-dimensional layers with uniform molecular orientation. Figure 1.2.1 shows how molecules aggregate into nematic or smectic phases. Note that the nematic phase is lacking a layered arrangement of molecules. The only order is the uniaxial orientation of molecules. This orientational order could be controlled by environmental conditions such as external electric field. A smectic phase has not only the unified molecular orientation but also a positional order that results from the phase separation of rigid and soft moieties of molecules. In some special cases, there also exists bond orientational order (e.g., hexatic B phase). At molecular level, rigid units which often feature aromatic moieties provide order for the system, while flexible substituents at the end(s) of a molecule are usually conformationally flexible and provide molecular mobility. A
unit building block that is mainly responsible for the generation of a LC phase is named as a mesogen. A mesogen could be one molecule, part of a polymeric molecule or a collection of molecules. The cubic mesophase is defined based on a distinctive three-dimensional cubic lattice.\textsuperscript{18}

\textbf{Figure 1.2.1.} Aggregation of molecules in a nematic phase (left hand side) and in a smectic phase (right hand side)
Gibbs free energy is the sum of contributions from enthalpy and entropy. The formation of crystalline lattice is driven by the maximization of inter-molecular (inter-atomic) interactions, which minimizes the energy of enthalpy. The isotropization process, on the other hand, is driven by the natural tendency of entropy maximization. As the entropy contribution is proportional to the temperature, it becomes more important as temperature increases. At a certain temperature, whether enthalpy or entropy dominates the minimization of the Gibbs free energy strongly depends on the state of matter. In a LC phase involving micro-phase segregation between rigid mesogens and soft, flexible tails (such as smectic, columnar and cubic LC phases), the enthalpy effect plays the major role in the rigid parts while the entropy contribution dominates in the soft
parts. The phase segregation is often aided by the different inter-molecular interactions experienced rigid parts and soft parts. Hydrogen-bonding, interaction between strong dipoles and $\pi-\pi$ interaction are stronger members of intermolecular interactions while Debye forces and London dispersion forces are much weaker. Examples can be found in nature illustrating the maximization of interactions (e.g., water oil separation). Water molecules interact with each other strongly mainly because of Hydrogen-bonding. As the result, oil molecules are excluded from water phase because the interaction between water molecules and non-polar oil molecules is much weaker. Such phenomenon is referred as phase separation (or phase segregation). When the separated phases are covalently bonded, micro-phase segregation occurs. The shape of the micro-phase segregated domains depends on the curvature of the interface between two domains. The interface curvature itself is mainly dictated by the cross-section areas of the two phase separated parts at the interface. While the interface is close to flat, the phase segregation results in the formation of a smectic phase. If one gradually increases the cross-sectional area of the soft part with respect to the rigid part, the micro-phase segregation may generate a gyroid phase, a columnar phase and even cubic spherical phase. In the cases of columnar and cubic spherical phases, the rigid mesogens is the dispersed phase.\(^{19}\).

Discotic LC phases feature a planar, usually $\pi$-conjugated (discotic) mesogen. Examples of molecules possessing structural element of discotic mesogens are shown in Figure 1.2.3. Those molecules usually have rotational symmetry that is higher than two-fold. Instead of being limited on only two ends for rod-like molecules, discotic mesogens have more substituents that are evenly distributed around the aromatic core.
Discotic LC phases can be further classified based on the order of the mesophase. As shown in Figure 1.2.4, molecules have only long-range molecular orientational order in a discotic nematic phase, while in a discotic columnar LC (DCLC) phase, molecules aggregate into column-like structures. Those columns further aggregate into a two-dimensional lattice based on much weaker inter-column interactions (Figure 1.2.5). The strong π-π interaction is the result of the balance of London dispersion force and the electrostatic attractive force of quadrupole-quadrupole interactions. Adjacent aromatic cores pack closely with the face-to-face distance typically in the range of 3.4 to 3.7 angstroms. Each column is wrapped with a mantle of non-aromatic parts of the molecule, usually being the soft peripheral substituents.
Many disc-shaped molecules with covalently fused rigid-soft moieties can potentially form columnar structures with or without the aid of intra-column $\pi$-$\pi$ interactions. In the latter case, the formation of columnar mesophase is mainly driven by rigid-soft phase separation as well as rigid-soft interfacial curvature. DCLC phases are of researchers’ great interest because of their special structural implication on charge transporting properties. Intra-column $\pi$ orbital
overlap allows hopping of charge carriers between adjacent aromatic cores. On the other hand, substituents which are usually based on alkyl or alkoxy chains are insulating and therefore hinder the inter-column charge carrier hopping. Consequently, columns in DCLC materials serve as one-dimensional charge transport channels. Charge carrier mobilities measured along the column axis direction is usually orders of magnitude higher than the other two dimensions. Unlike the crystalline phase in which every atom is restricted with little motional freedom, molten, fluid-like side chains in a DCLC phase give rise to the ability of self-healing, self-organization and the ability to respond to external stimulus. Self-organization allows aligning of column axes perpendicular to the substrate by slow cooling from melted isotropic liquid or annealing at temperature approaching the clearing point. Facile solution processing approach has also been reported for materials in their DCLC phase to align column axes to be parallel to the substrate. In both cases, the molecular mobility of substituents enables DCLC materials to sample the free energy difference and to rearrange themselves towards the thermodynamically favored states. These features have made it possible to obtain highly uniform molecular orientation over a large area of device substrate. Due to the anisotropic charge transport nature of DCLC materials, it is essential that we can control the major conducting direction as desired. In FETs with DCLC materials as the active component, the column axis should be parallel to the dielectric substrate. On the other hand, applications like organic light emitting diodes (OLEDs) or photovoltaic (PV) cells prefer the conducting direction to be perpendicular to electrode substrates.

1.3. Engineering of discotic columnar liquid crystalline phase

Compounds containing aromatic moieties have been under intense investigation in order to understand their thermo behaviors and study their performance as charge transport materials.
Dozens among those useful “cores” have been taken a step further to make their corresponding derivatives in order to explore their DCLC phase properties. Those compounds include: triphenylenes, pyrenes, perylenes, porphyrins, phthalocyanines, hexabenzocoronenes, and other graphene-type molecules with even larger conjugated aromatics and so on (Figure 1.3.1).

![Molecular structures of common aromatic conjugates whose derivatives are under intense investigations](image)

Figure 1.3.1. Molecular structures of common aromatic conjugates whose derivatives are under intense investigations

The common strategy for creating mesophase for those cores is based on the rigid-soft segregation between the aromatic moieties with build-in rigidity and the liquid-like flexible segments at the periphery. Driven by co-facial $\pi-\pi$ interaction and non-flat interface curvature, molecules aggregate to form column-like structures. Those columnar aggregations further arrange into a two-dimensional lattice with long range positional order. Since space between
adjacent columns must be occupied without vacancy, the space filling ability of flexible chains is of particular importance to the formation of a DCLC phase. Such ability may come from the bulkiness of side chains, number of substituents, the substitution symmetry of the molecule, or the combination thereof. Examples of DCLC molecules are shown in Figure 1.3.2.
n=0: Cr -10 Colh 360 Iso
n=1: Cr -10 Colh 226 Iso

n=2: Solid 244 Colh 313 Iso
n=3: Cr 193 Colh 287 Iso
n=4: Cr 161 Colh 242 Iso
n=5: Cr 114 Colh 203 Iso
n=6: Cr 72 Colh 177 Iso
n=7: Cr 63 Colh 152 Iso
n=8: Cr 62 Colh 132 Iso
n=9: Cr 60 Colh 100 Iso

R=C_{nH_{2n+1}}
Most common configurations that lead to a DCLC phase include a high rotational symmetry, incorporation of linear alkyl side chains, multiple substitution sites (usually three to eight), and azimuthally uniform angular distribution of flexible chains. The incorporation of alkyl chains are required to provide the molecule with mobility. However, the motion of the melted tails may disturb the $\pi$-stack and lead to stronger fluctuation in molecular order. The order of columnar stacking could be reflected by the clearing point (the temperature at which a LC phase turns into an isotropic liquid) and other factors. For most of compounds, clearing point decreases as the length of side chains increases due to greater molecular mobility.\textsuperscript{21} This attribution is reflected by the charge carrier mobility study of triphenylenes derivatives. The free carrier mobility decreases with the increase of chain length. However, adding a gelator suppresses the molecular fluctuation in the LC mesophase and lead to mobility data that is almost independent of the size of substituents.\textsuperscript{17,22} In most of cases, generating LC phase (from a crystalline phase) reduces the $\pi$-stacking order. At the same time, it is necessary to control this disturbance so that it’s not overly large to severely undermine the stability of the LC phase. This is especially true with the use of branched substituents without a spacer (Figure 1.3.3).\textsuperscript{23} Because of the long branched alkyl chains, the branching carbon has a high rotational freedom.\textsuperscript{2} Such substituents are more powerful in space filling but also cause much more steric hindrance, which could translate into a much lower clearing point. The result is that the crystalline phase would melt into the corresponding DCLC phase at a much lower temperature (near RT) while the clearing point of the compound also decreases substantially. One solution is to use alkoxy or
alkanoyloxy substituents as it leads to much wider mesophase range instead of a simple shift towards lower temperature.\textsuperscript{24} Compared to sp\textsuperscript{3}-hybridized carbon-carbon bond, a sp\textsuperscript{3}-hybridized carbon-oxygen bond has a lower rotational barrier. It is believed that oxygen atoms can serve as a linker which to some extent decouples the motion of side chains from the orderly packing of π-systems by spatially separating two parts of the molecule.\textsuperscript{25} The strategy allows the incorporation of side chains with greater mobility while retaining or even improving the order of π-stacks. Application of longer linkers combining with other approaches had widened the possibility for many more aromatic systems to become members of DCLC materials. It should be noted that the coupling of the side chain motion and ordered π-units aggregates in the DCLC phase may lead to substantial decrease in charge carrier mobility compared to the corresponding crystalline phase.\textsuperscript{26} The structural disorder of the intra-column packing should be considered as the major drawback of DCLC materials used for charge transport.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{molecule.png}
\caption{Molecular structure of DCLC hexabenzocoronene featuring branched side chains}
\end{figure}

It is also desirable to have the ability to control the volume or weight ratio of the aromatic part to the aliphatic part. While the aliphatic tails are providing necessary molecular mobility and filling up the space, it is only the aromatic part that contributes to the optoelectronic
properties of the material. Therefore, less bulky side groups are favored as they make the molecule more atomic efficient when used as active component in application.

There are mesogens that tend to form a smectic phase or crystalline phase such as perylene tetracarboxylic diimide (PDI). Compared to other discotic mesogens, it is more rod-like instead of disk-like especially considering only two ends of the molecule is available for side chain substitution (Bay area substitution is possible but not desirable for its less synthetic accessibility, the altering of HOMO and LUMO energy levels and the negative effect on $\pi$-stacking). Except for using bulky atomic inefficient substituents with structure as shown in Figure 1.3.2, oligoethylene glycol (OEG) units have been found to be able to give rise to DCLC mesophase (Figure 1.3.4). This is due to the high conformational flexibility of OEG tails that enable the efficient wrap of the column surface.\textsuperscript{27} OEG tails were introduced as branched imide groups because the number of connection available for substituents is limited.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure1.3.4.png}
\caption{Molecular structure of DCLC PDIs featuring branched OEG side chains}
\end{figure}

Dendrons have also been found to be powerful molecular moieties to induce DCLC phases.\textsuperscript{25,28} Examples are shown in Figure 1.3.5. The application of dendrons has broadened the range of organic materials that could form a DCLC phase with promising optoelectronic properties. The driving force of the columnar phase formation comes from the fan shape of the dendron tails. Linkers such as an OEG segment were employed in order for $\pi$-stacks to be preserved. Despite of its versatility, the strategy does not work very well with large $\pi$-conjugated units.
Supplementary interaction other than π-π interaction (strength ranges from 0 to 50 kJ/mol$^{29}$) could be utilized to construct novel DCLC mesogen or to improve the intra-column
order. For instance, the intra-column intermolecular dipole-dipole interaction between nearby methoxy groups is thought to be responsible for the formation of the highly ordered helical columnar phase.\textsuperscript{1} Similar effects have also been observed with H-bonded discotic molecules where amido or ureido groups form intra-column inter-molecular H-bonds which substantially increase the intra-column positional order.\textsuperscript{30} Moreover, the non-tilted core packing from DCLC phase could be preserved in the low-lying crystalline phase instead of forming the commonly seen herringbone packing. Generally speaking, incorporation of supplementary forces increases the overall inter-molecular interaction and stabilizes the mesophase by increasing the order of packing. In a special case, the dipole-dipole interaction between anhydride groups of aromatic moieties leads to the formation of a DCLC phase with interdigitated intra-column molecular packing.\textsuperscript{31}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{molecular_structure.png}
\caption{Molecular structure of supplementary interaction incorporated DCLC materials}
\end{figure}
Rotation of mesogen is one important subject of study since the overlapping of the frontier orbitals are closely related to the relative angular position of adjacent \( \pi \)-units. The helical intra-column packing as resulted from rotation has strong influence on two aspects. First, helicity is usually associated with improved molecular packing and thus lead to a more stabilized LC phase.\(^{32}\) Second, we have learned from theoretical calculations that the rotational angle between adjacent \( \pi \)-units strongly affects the p-orbital overlap which further affects charge transport.\(^{33}\) There have been many examples of helical systems with columnar structures. Driving forces responsible for the formation of such systems are various. It is observed that meta-trimethoxy functionalized hexahenzocoronene (HBC) forms helical columnar structures with a rotational angle of ca. 4.28°, which is due to the inter-molecular dipole-dipole interaction between methoxy groups (Figure 1.3.7).\(^{1}\) Other examples based on the same driving force include the hexahexylthiotriphenylene compound which forms highly ordered helical columnar LC phase without macroscopic grain boundaries.\(^{17, 34}\)
Introducing bulky groups near the aromatic core causes steric hindrance and forces the molecule to rotate. Examples are alkylphenyl substituted HBCs (Figure 1.3.8). The phenyl group directly connected to the aromatic core rotates out of the HBC plane. To accommodate the extra steric demand while still holding the π-stack, the molecule has to rotate at an angle of 20°. Further adjustment to the rotation angle could be achieved by incorporating more extended rigid groups. Replacing alkyl chains with tolane units causes the rotation angle to decrease to 15°. It is important to control the size of groups that provide steric hindrance to the system so that it is not too small to be ineffective neither too big to destroy the columnar packing.
Figure 1.3.8. Alkylphenyl substituted hexabenzocoronenes which aggregates into DCLC phase with a 20° or 15° rotational angle

Tuning the helical rotation within the column can also be realized by changing the substitution layout on the aromatic core. As shown in Figure 1.3.9, the aromatic core rotates 60° with respect to its neighbor molecules when there are six alkyl chain substitutions. Removing the bay area alkyl chains alters the rotation angle to 90°. The increase of the angle is due to the larger space filling requirement from larger number of side chains.\(^{36}\) The helical rotation in the columnar structure was also observed in other aromatic systems such as perylene, terrylene,quaterrylene and coronene diimide. It has been shown that the intra-column rotation angles in the columnar structure of those compounds with the same alkyl substitutions are identical and independent of the core size.\(^{37}\) However, the 4\(_1\) helix is replaced by a staggered packing mode when replacing the alkyl groups with polyethylene glycol (PEG) chains.\(^{38}\) In this case, it is likely that the higher conformational freedom and larger cross sectional area of the PEG
segments leads to an increased rotation angle. Single-sided substitution pattern is the extreme case of poor substitution symmetry leading to helical columnar structures. Examples are dendron functionalized polycyclic aromatic hydrocarbons, and partially stripped hexa-peri-HBCs and so on.\textsuperscript{25, 27, 39} Aromatic cores have to rotate to uniformly accommodate side chains and meet with the space filling requirement.

![Chemical structure](image)

**Figure 1.3.9.** Chemical structures of example compounds showing the different rotation angles (60° and 90° for upper and lower substitution patterns, respectively) based on different substitution layout.

Another alternative way of tuning the rotation angle is to utilize the phase separation. One example is shown in Figure 1.3.10. The semi-triangular-shaped aromatic core which is substituted with branched alkyl chains exhibit a rotation angle of 40° due to the steric hindrance provided by phenyl groups. In contrast, the alkyl and PEG alternatingly substituted compound displays a rotation angle of 60° due to the hydrophilic and hydrophobic interactions.\textsuperscript{33, 40}
Organic semiconducting materials are mostly based on aromatic hydrocarbons which by their own are hard to utilize. Incorporation of flexible side chains may provide enhanced solubility, induce columnar packing of disc-shaped molecules, allow the control of macroscopic molecular alignment, enable self-organization and self-healing, and tune the intra-column molecular aggregation. Topics of the engineering of substitutions include the nature of the tail,
the length and branching degree of the tail, the substitution pattern, and types of the connection to the aromatic core. On the other hand, as the part of the molecule which is responsible for the charge transport, aromatic cores with larger \( \pi \)-conjugated systems usually have stronger \( \pi-\pi \) interaction and greater electronic coupling. However, those larger aromatic cores are synthetically less accessible and less soluble.

1.4. References


19. (a) N. Boden, R. J. B., and J. Clements, Mechanism of quasi-one-dimensional electronic conductivity in discotic liquid crystals. J. Chem. Phys. 1993, 98, 5920; (b) Anick M. van de Craats, J. M. W., Dr. Matthijs P. de Haas, Dr. Dieter Adam, Dr. Jürgen Simmerer, Prof Dietrich Haarer, Dr. Peter Schuhmacher, The mobility of charge carriers in all four phases of the columnar discotic material hexakis(hexylthio)triphenylene: Combined TOF and PR-TRMC results. Adv. Mater. 1996, 8, 823-826.


39. (a) Jonathan P. Hill, W. J., Atsuko Kosaka, Takanori Fukushima, Hideki Ichihara, Takeshi Shimomura, Kohzo Ito, Tomihiro Hashizume, Noriyuki Ishii, Takuzo Aida, Self-Assembled
CHAPTER 2. BUNDLED-STACK DISCOTIC COLUMNAR LIQUID CRYSTALLINE PHASE: INSULATED MULTI-STRAND NANOWIRES

2.1 Introduction

Discotic columnar liquid crystalline (DCLC) materials with a conjugated mesogen have been under intensive investigation due to their potential applications in a number of fields including charge and energy transport. In a DCLC phase, the rigid conjugated discotic mesogens are micro-phase segregated from flexible peripheral chains, forming conducting \( \pi \)-stacks as the cores of supramolecular columns that are surrounded by flexible chains. These columns then pack into a two-dimensional (2D) long-range ordered lattice. In vast majority of DCLC molecules the mesogen is symmetrically surrounded by flexible chains, thus in a DCLC phase there is only a single conducting \( \pi \)-stack per column. One-dimensional (1D) charge carrier migration in such a phase is vulnerable to the occurrence of defects. As suggested by Müllen et al., the charge transport robustness of a DCLC phase can be substantially improved if each column encompasses a bundle of conducting \( \pi \)-stacks with the stacking axes parallel to the column axis, as defects in a \( \pi \)-stack can be circumvented by moving to another \( \pi \)-stack in the same bundle to continue charge transport (schematic drawing of electron movement in Figure2.1). This requires that there are no insulating moieties blocking intra-bundle inter-stack charge hopping. Such a bundled-stack DCLC (BSDCLC) phase is essentially a nanometer-sized version of insulated multi-strand conducting wires. Here we report the first BSDCLC material showing high charge carrier mobility.
A columnar phase involving multiple $\pi$-stacks per column has been proposed for self-assembling semifluorinated dendrons with a conjugated charge transport unit attached to the apex.\textsuperscript{4} However, this phase is usually not considered as a DCLC phase since the self-assembly is strongly influenced by the fluorophobic effect and a discotic mesogen is not needed for the formation of a columnar phase.\textsuperscript{5} Moreover, only relatively small charge transport units can be accommodated in such a multi-stack columnar structure,\textsuperscript{4c} which results in limited charge carrier mobility.\textsuperscript{6} Very recently, a five-stack per column structure has been proposed for a DCLC chlorophyll derivative.\textsuperscript{7} In this case, direct intra-column inter-stack contact is obstructed by peripheral methyl and ethyl groups. To form a true BSDCLC phase, it is necessary to remove some flexible chains from a conventional DCLC molecule to expose the discotic mesogen to intra-column inter-stack mesogen-mesogen contact. Although the synthesis and characterization of “partially unwrapped” discotic molecules have been reported, a BSDCLC phase was not identified.\textsuperscript{3a}
2.2. Molecular design

We chose perylene tetracarboxylic diester monoanhydride (PEA) as the candidate of mesogen of a BSDCLC phase for several reasons. First of all, unlike perylene as a molecule that is fully surrounded by C-H bonds at the periphery, anhydride group in PEA is fully open. Furthermore, the anhydride part is at the farthest end of the long axis of mesogen with respect to the substituent. This arrangement is likely to ensure the direct contact between charged mesogens with minimum distance and barriers that charge carriers have to hop over provided the desired BSDCLC phase is formed. Secondly, it is synthetically easy to attach different substituents to the ester part of the mesogen. Finally, perylene is known to have strong π-stack formation tendency. To encourage the formation of a DCLC phase, two bulky branched alkyl chains were installed, giving PEA 1 shown in Figure 2.2. Assuming a 3.5 Å π-stacking distance, the cross-sectional area of a π-stacked perylene ring is ~ 32.0 Å². At the same time, four n-alkyl chains in 1 feature a collective lateral area of ~ 80 Å². With such a finite mesogen/flexible chain interfacial curvature, a DCLC phase with mesogen cylinders embedded in an alkyl continuum is anticipated.

![Molecular structure of compound 1](image)

Figure 2.2. Molecular structure of compound 1

2.3. Results

2.3.1. Thermal behavior and phase structure
1 is stored at RT for over 18 months and no impurities were found by $^1$HNMR due to degradation. The compound is soft and easy to align under mechanic shearing force. 1 is a dark red sticky compound, melts at around 203 °C with a small heat of fusion ($\Delta H = 4.1$ kJ/mol). Differential scanning calorimetry (DSC) and polarizing light microscopy (PLM) were first utilized to probe its phase transition behaviors. The DSC traces are shown in Figure 2.3a. The endothermic peak with the onset at 204.0 °C ($\Delta H = 4.5$ kJ/mol) during heating can be attributed to the isotropization process as confirmed by PLM results. The dendritic texture presented in Figure2.3b is indicative of the formation of a DCLC phase upon cooling from the isotropic liquid state, which is in agreement with the associated exothermic enthalpy value ($\Delta H = 4.1$ kJ/mol) and the small undercooling (onset at 202.6 °C , $\Delta T= 1.4$ °C) needed for the development of the phase from liquid. The fact that there are no transitions between room temperature (RT) and the isotropization temperature suggests that 1 is a RT DCLC material. It should be noted that the area that is dark under microscope would turn bright upon horizontal rotation of sample plane. This observation suggests that the column axis is not always perpendicular to the substrate.

**Figure 2.3.** (a) First cooling and second heating DSC traces of 1 at a ramp rate of 20 °C/min. (b) PLM micrograph of 1 taken at 202.0 °C after slowly cooled from the isotropic liquid state.
The discotic columnar liquid crystalline phase is verified by the RT 1D X-ray diffraction (XRD) pattern shown in Figure 2.4a. The ordered nature of the phase is testified by the appearance of multiple sharp diffraction peaks at the small-angle region. Those diffractions hold the information about the electron density variations in structures on a relatively large scale (up to several nanometers). As found in this 1D integration pattern, d-spacings of small angle diffractions have ratios of 1:3:4:7:9 etc., which indicates the hexagonally packed structure. In contrast, the absence of sharp diffraction peaks between 1.3 and 1.7 Å\(^{-1}\) has indicated that the alkyl chains are in a disorder, liquid-like state. On the other hand, wide angle diffractions reflect structures on a much smaller scale (several angstroms). As shown in the pattern, the peak at 1.742 Å\(^{-1}\) (d-spacing = 0.3606 nm) can be attributed to the π-stack of perylene units. Because directions along which the electron density changes are different for columns π-stacks, on a mechanically sheared fiber pattern, one can easily discriminate diffractions from both structural elements by seeing them on different axis. As shown with figure 2.7, the diffractions on the meridine axis contain information about π units stacking while on the equatorial axis, the information is all about the 2D packing of columns.
Figure 2.4. (a) 1D XRD pattern of 1 at RT with small-angle diffractions indexed. Insets show the weak small-angle diffractions (red) and the peak arising from π-stacking order. The peak marked “Si” corresponds to the diffraction from crystalline silicon powder that were added as the calibration standard. (b) 2D XRD powder pattern of 1 at RT with Si powder as the internal reference.

The small-angle diffractions in Figure 2.4a were indexed as (10), (11), (20), (21) and (30) diffractions of a 2D hexagonal lattice with a = 4.346 nm. This assignment was confirmed by the six-fold symmetry of the 2D small-angle XRD pattern shown in Figure 1f with the incident X-ray along the column direction, thanks to the appreciable tendency of 1 to self-organize into millimeter-sized domains with homeotropically aligned columns when cooled slowly from the liquid state. Comparing the pattern shown in Figure 2.5 with ones in Figure2.3a and Figure2.3b, all diffractions caused by the π-stack of perylene units dissapeared but left with single-crytal-like small angle diffractions. In this way, the hexagonal columnar packing could be strongly supported and viewed in a much straight forward manner. The correlation length of the 2D lattice along the 10 direction is more than 100 nm, as estimated from the width of (10) diffraction using the Scherrer equation,$^{13}$ showing the long-range ordered hexagonally packed supramolecular columns.
Figure 2.5. 2D small-angle diffraction pattern of 1 at RT (the incident X-ray beam parallel to the column axis).

The formation of π-stacks is also supported by fluorescence spectra of 1 depicted in Figure 2.6. The spectrum of 1 in a dilute chloroform solution features three bands peak at 523, 567 and 618 nm, in the order of decreasing intensity. These bands can be attributed to one electronic transition of unassociated 1 molecules coupled with vibrational transitions, similar to what has been suggested for perylene diimdes. However, in the RT DCLC phase, the λ_max red-shifted by more than 120 nm to 650 nm, indicating extensively π-stacked perylene units.
2.3.2. Identification of BSDCLC phase and its intra-columnar structure

To extract more in-depth structural information, a 2D XRD pattern was collected on a well-aligned 1 which was readily prepared by mechanical shearing, due to its RT DCLC nature. As displayed in Figure 2.7, the series of diffractions on the equator originate from supramolecular columns well-aligned along the shearing direction. The diffused halo with $d \approx 0.45$ nm suggested that the alkyl chains don’t have clear preferential orientation despite oriented columns, which is in agreement with their liquid-like character. The strongest diffraction on the meridian at $d = 0.3606$ nm can be assigned to $\pi$-stacking order of perylene units. The fact that this diffraction does not split means that discotic mesogens are perpendicular to the column axis. Had only one perylene $\pi$-stack involved in each supramolecular column, the density calculated from given cell parameters would be 0.305 g/cm$^3$. However, the measured value is $1.027 \pm 0.001$ g/cm$^3$. To match the experimental density value, about 3.4 $\pi$ stacks in each column are needed. Such an intra-column structure should be responsible for the appearance of those diffused scatterings on the meridian and in the quadrants. The meridian scattering maxima can be indexed as $(001), (002), (004), (005)$ and $(006)$ reflections, as shown in Figure 2.7a. Note that
(005) reflection originates from the inter-ring spacing of π-stacked perylene units, which implies that cell parameter \( c = 1.803 \) nm. In other words, there are five stacked 1 molecules along the stack/column axis in each cell. In addition to these meridian scattering maxima, there are a few weak scatterings in quadrants on first, second and third layer. Although there are a relative large number of diffractions, the phase is still a liquid crystalline instead of a crystalline phase since all quadrants diffractions are very diffuse indicating the lack of three-dimensional (3D) crystalline order.

**Figure 2.7.** (a) 2D XRD pattern of a shear-oriented 1 with the incident beam along the thickness direction. (b) Simulated X-ray fiber pattern of 1 in the composite structure shown in Figure 4c.

The arrow marks the shear /fiber (for the simulated pattern) direction.
One unique feature of the 2D diffraction pattern is the unprecedentedly large number of meridian diffraction maxima for a DCLC phase. This calls for a structure with appreciable electron density variations in the unit cell along the column axis direction other than what arises from the regularly $\pi$-stacked perylene rings. With this in mind, a bundled-stack intra-column structure involving two $\pi$-stacking modes is proposed.

**Figure 2.8.** Schematic of a unit cell showing bundled-stack intra-column organization of mesogens.

The packing scheme of mesogens is shown in Figure 2.8. Each unit cell contains 17 mesogens arranged in 5 strata. 9 of them form a bundle of 3 $\pi$-stacks in 3 strata. Inside each stack, the mesogen rotates around its plane normal with respect to the neighboring mesogen in the same stack and the direction of rotation alternates along the stacking axis. The remaining eight mesogens organize into a bundle of four $\pi$-stacks in two strata as shown in Figure 2.8. The separation between adjacent perylene $\pi$-systems along the column axis direction is always
0.3606 nm. This model has a calculated density of 1.037 g/cm³ which agrees with the experimental value. Moreover, the contrast between the three-stack and four-stack regions can provide the needed electron density variation.

To test the validity of this intra-column organization model, molecular modeling was carried out using Cerius 2. Because the diffraction data indicated that alkyl chains are disordered, they were replaced by 2-methyl propyl groups, giving the model compound 1M (figure2.9). When the formation of perylene π-stacks is concerned, a 2-methyl propyl group has essentially the same steric demand as the branched alkyl group in 1. Therefore both the mesogen-related interactions and flexible chain steric hindrance of 1 involved in intra-column organization can be well represented by 1M.

![Molecular structure of 1M](image)

**Figure 2.9.** Molecular structure of 1M

Since the proposed structure can be viewed as a composite structure that consists of two parts with different stacking modes, unit cells containing three and four π-stacks of 1M molecules were constructed and energy-minimized separately as the first steps. As shown in Figure 2.10, the intra-stack rotation angle is ~99° for both three-stack and four-stack structures. Packed 1M molecules have an average potential energy which is 163 (three-stack) or 177 (four-stack) kJ/mol lower than an isolated 1M molecule, due to attractive intermolecular interactions. Subsequently, 1M molecules in both stacking modes at their respectively energy-minimized conformation were combined into the proposed structure which is then energy-minimized and
shown in Figure 2.10c-f. The simulated diffraction was generated from a single column in the energy-minimized composite structure and shown in Figure 2.7b. The good agreement between experimental intra-column diffractions and the simulated pattern, especially meridian diffractions, underscores the validity of the proposed composite structure. As shown in Figure 2.10, each conjugated mesogen has direct contact with two mesogens in neighboring stacks, which qualifies this phase as a genuine BSDCLC phase.

**Figure 2.10.** Energy-minimized unit cells viewed along the column axis (except (d) which is a side view). (a) three-stack structure. (b) four-stack structure. (c)-(f) composite structure with the three-stack part (three strata) on the top. Scale bars represent 2 nm. For the composite structure, all peripheral groups were removed for the sake of clarity. Molecules were shown in cylinder models, except in (a), (b), (e) and (f), molecules in the second stratum were shown in space
filling models as a means to indicate inter-stack mesogen contact and intra-stack rotation angles.

Molecules in (c) and (d) were colored stratum-wise: the default color scheme for 1\textsuperscript{st} and 3\textsuperscript{rd} stratum; red, blue, green for 2\textsuperscript{nd}, 4\textsuperscript{th} and 5\textsuperscript{th} strata, respectively. (e) and (f) show the views from the four-stack and three-stack ends of the composite cell, respectively.

The calculated average potential energy of 1\textbf{M} molecules in the composite structure is 159 kJ/mol below that of an isolated 1\textbf{M}, which indicates that 1\textbf{M} molecules are experiencing fairly strong attractive intermolecular interactions. However, such interactions are slightly weaker than those in a simple three-stack or four-stack structure, likely due to the energy cost arising from the inevitable packing discontinuities at three-stack/four-stack interfaces. This suggests that the long, flexible alkyl chains should play the key role in driving the formation of the composite structure instead of a simple three-stack or four-stack structure which is more enthalpically favored if long alkyl chains are not considered. We speculate that when packed in the simple three-stack structure, the n-alkyl\textsuperscript{14} chains of 1 have to adopt a conformation with a relatively large number of gauche dihedrals, which comes with an enthalpy cost leading to a higher free energy. Conversely, when packed in the four-stack structure, the n-alkyl chains suffer too few gauche dihedrals, resulting in an entropy penalty. By combining three- and four-stack modes, n-alkyl chains are in a conformation with free energy advantage that is more than enough to compensate for the energy cost from the packing discontinuities in the composite structure and makes it the most stable one.\textsuperscript{15} This analysis leads to an important implication that peripheral flexible chain engineering may be applied to generate a single-stacking-mode BSDCLC phase.

In order to examine our speculation on the cause of large $\pi$-stacking spacing, we synthesized compound 2 which has the structure shown in Figure 2.11. Compared to compound
1, the incorporated swallow tail has a symmetrical structure with much shorter chain length (approximately half of the tail as used in 1). However, from the analysis of the XRD pattern as shown in Figure 2.12, the π-stacking spacing was determined to be 0.3605nm which is almost identical to the value obtained for compound 1. This finding has supported our argument that the branching carbon of the swallow tail is the main reason for the largely separated intra-column molecular packing.

![Figure 2.11. Molecular structure of 2](image)

**Figure 2.11.** Molecular structure of 2

![Figure 2.12.](image)  
(a) 1-D XRD pattern of 2 at RT  (b) 2D XRD pattern of a shear-oriented 2 with the incident beam along the thickness direction.

Although the formation of the BSDCLC phase is partly driven by the large space filling requirement of the swallow tail, the contribution from the aromatic core is not negligible. The
anhydride structure is considered to be an important role in the phase formation as it is capable of forming strong inter-molecular dipole-dipole interaction. Replacing the anhydride group with different imide groups will help us better understand the influence of this additional force. Compound 3 and compound 4 were synthesized and their structures are shown in Figure 2.13. Compound 3 was designed to incorporate an imide group which has the ability to form H-bond with carbonyl groups. Compound 4 was designed to decrease the dipole moment of the polar group and to force a further distance separating two adjacent imide groups.

![Molecular structure of 3 and 4](image)

**Figure 2.13.** Molecular structure of 3 (top) and 4 (bottom)

2-D XRD patterns of sheared samples of 3 and 4 are shown in Figure 2.14. For both compounds, hexagonally arranged columnar structure could be identified. Moreover, density measurements have suggested more than one stack in a single column. Therefore, we concluded that despite of obvious structural differences, both compounds exhibit bundled-stack columnar aggregation. While compound 3 forms BSDCLC phase, compound 4 has a 3D crystalline lattice.
Introducing H-bonds to the BSDCLC phase has a profound influence on the phase structure. The most apparent change on the oriented 2-D XRD pattern of compound 3 is the splitting of meridinal diffractions originated from π-stack. This observation has suggested that instead of having the plane of aromatic core perpendicular to the columnar axis, the intra-columnar packing is tilted. In contrast, replacing the imide hydrogen with a methyl group leads to a three-dimensional crystalline structure. It is speculated that the inter-core interaction is substantially weakened due to the reduced polarity of carbonyl groups, the inability of forming H-bonds and the further distance between aromatic cores within the same strata. While the phase structure is greatly varied as the consequence of changing the inter-core secondary interactions, we also see that the formation of bundled-stack structure is independent of the anhydride group.

2.3.3. Structural defections and possible improvements
There are two drawbacks in the structure of the BSDCLC phase of 1 as a charge transport material. The first one is the presence of packing discontinuities at three-stack/four-stack interfaces. The second is the relatively large \( \pi \)-stack spacing (0.3606 nm), probably due to the steric hindrance of the \( \text{sp}^3 \) hybridized branching point in the long alkyl peripheral chains. In the absence of steric-demanding substituents, the inter-planar spacing of cofacially stacked perylene rings is typically between 0.34 and 0.35 nm in a DCLC phase of perylene tetracarboxylic derivatives including diimdes,\(^{16}\) tetraesters\(^{17}\) and monoimide diesters.\(^{18}\) A larger spacing is associated with a weaker intermolecular \( \pi \)-orbital coupling which tends to result in a lower charge carrier mobility.\(^{19}\) Moreover, in comparison with the most widely studied DCLC perylene diimides, 1 also suffers from a smaller \( \pi \)-conjugated discotic mesogen as the two ester carbonyl groups are not coplanar to the perylene ring.\(^{20}\) Nevertheless, 1 exhibits respectable charge carrier mobility in its RT BSDCLC phase. The sum of 1D charge carrier mobility, as measured by pulse-radiolysis time resolved microwave conductivity technique (PR-TRMC), is \( 5.41 \times 10^{-2} \text{ cm}^2\text{V}^{-1}\text{s}^{-1} \), fully comparable to those high mobility values\(^{16a,b,21}\) that have been determined by PR-TRMC for DCLC perylene diimides with tight \( \pi \)-stacks, despite the abovementioned drawbacks. This performance unquestionably attested the distinct structural advantage and potential of a BSDCLC phase in providing high charge carrier mobility. Note that even higher charge carrier mobility is anticipated for BSDCLC PEAs with a single stacking mode (therefore no packing discontinuities) and/or tight \( \pi \)-stacks.

2.4. Conclusions

We have designed and synthesized PEA 1, the first compound that displays a BSDCLC phase. Structure characterizations and simulation results revealed that it self-assembles into a
unique composite BSDCLC phase involving two stacking modes at RT. Although the direct relationship of enhanced charge carrier transport and the novel BSDCLC structure has yet to be established, we indeed observed the charge carrier mobility as one among the best values found for perylene derivatives despite the abovementioned tremendous drawbacks the system beholds. The incorporation of BSDCLC structure with mesogens exhibiting semiconducting properties may potentially be a fundamental solution towards enhancing the organic semiconductor’s electronic performance. Tuning the structure of flexible peripheral chains may lead to BSDCLC phases with a single stacking mode and tightly π-stacked mesogens which is expected to exhibit even better charge transport performance. On a more general basis, the application of this design principle to other DCLC mesogens may generate a variety of BSDCLC materials with improved charge transport characteristics.

2.5. Experimental section

**Instruments and characterizations**

$^1$H NMR and $^{13}$C spectra were recorded on a Varian 600 MHz NMR spectrometer, with deuterated chloroform (CDCl$_3$) as solvent at 25 °C. The chemical shifts were reported using chloroform as the internal standard. The $^1$HNMR and $^{13}$CNMR graphs and data were scanned and calculated from original graphs.

High resolution mass spectrum (HRMS) of 1 was obtained in Chemistry Department at Rutgers University Newark on an Apex-ultra 70 hybrid Fourier Transform mass spectrometer (Bruker Daltonics).

FT-IR spectra were collected on a Bruker Vertex 70V spectrometer at a resolution of 4 cm$^{-1}$. 
Fluorescence spectra were obtained on a JOBIN YVON Co. FluoroMax-3 spectrofluorometer with slits setting at 1 nm for excitation and 5 nm for emission, respectively. The excitation wavelengths were at 507 and 500 nm, for solution and solid measurements, respectively. Fluorescence spectra shown in Figure 1 were collected from the chloroform solution of 1 with a concentration of $2.10 \times 10^{-6}$ mol L$^{-1}$, as well as from the neat sample which was heated to isotropic state on a quartz plate and then allowed to cool to RT before the measurement.

All XRD measurements were performed at RT on a Bruker Nanostar instrument with a Cu K$_\alpha$ source. A VÂNTEC 2000 2D detector and an image plate were used as small and wide angle detectors, respectively. All samples of 1 for XRD studies were prepared by first heating up to isotropic liquid state, then cooling down to RT. The wide angle powder diffraction pattern shown in Figure 1 was collected from 1 mm thick 1 sample with Si powder as internal d-spacing reference. The 2D small angle diffraction pattern shown in Figure 1 (and Figure S3) was obtained by aligning the X-ray incident beam along the axis of supramolecular columns in a millimeter-sized homeotropically aligned single domain liquid crystalline sample of 1. The sample was prepared by cooling 1 (sandwiched between two fresh cleaved sodium chloride plates) from the isotropic liquid state stepwise (step size 0.1°C) to the temperature that texture started to develop. The cooling rate was then constantly adjusted to ensure the slow and complete development of the single domain. Consequently, the sample was ramping to RT at 5°C/min followed by dissolving sodium chloride in water. The diffraction pattern shown in Figure 2 was obtained by aligning the incident X-ray beam perpendicular to the plane of a mechanically sheared film of 1 with the shearing direction pointing upwards.

Polarized light microscopy picture shown in Figure 1 was taken from a Leica DM LB2
microscope equipped with a Leica DGC 320 camera and a Mettler Toledo FP82HT hotstage (controlled by a Mettler Toledo FP90 central processor). The sample of 1 was heated up to the isotropic liquid state then cooled down to 202.0°C with a cooling rate of 0.1°C/min.

DSC experiments were performed on a Perkin-Elmer PYRIS Diamond differential scanning calorimeter. Transition temperatures were determined using the onset temperatures and were calibrated using standard material (indium).

The mobility of charges in PEA 1 was determined by PR-TRMC measurements. PR-TRMC technique has been extensively described elsewhere. Briefly, the sample is irradiated with a short pulse of high-energy (3 MeV) electrons from a Van de Graaf accelerator, which leads initially to a low (micromolar) concentration of positive and negative charge carriers uniformly distributed in the irradiated medium. After the incident pulse (1 – 50 ns duration), the conductivity of the sample is probed as a function of time by monitoring the attenuation of a reflected microwave power (frequency range between 28 and 38 GHz, maximum electric field strength in the sample 10 V/m). The fractional change in microwave power reflected by the cell is directly proportional to the change in conductivity, $\Delta\sigma$. The concentration of charges that is generated initially can be estimated using dosimetry measurements combined with a charge-scavenging model. The sum of the 1D intracolumnar charge carrier mobilities from the dose-normalized radiation-induced conductivity at the end-of-the-pulse, $\Delta\sigma/D$, is determined according to the following equation:

$$\Sigma\mu = 3\frac{\Delta\sigma E_p}{D W_p}$$

where $E_p$ average energy absorbed per electron-hole pair formed and $W_p$ is the probability that initially formed ion- pairs survive until the end of the pulse. The value of $E_p$ is generally assumed to be ca. 25 eV and the value of $W_p$, acquired as described in ref.3, was 0.459. Because
both positive and negative charge carriers can contribute to the conductivity signal, \( \Sigma \mu \) represents the sum of hole and electron mobility.

**Materials and synthesis**

All reagents and chemicals were purchased from Fisher Scientific, Aldrich and VWR international and used as received. ALIQUAT 336 was kindly provided by Cognis Corporation.

The swallow tail was synthesized partly according to a literature procedure.\(^{22}\)

**Diethyl 2,2-dihexylmalonate**

The reaction system was protected by Argon during entire operation. Caution was taken to prevent moisture from coming inside the reaction container. Into a 500 ml round-bottomed flask were charged with 20.030 g (125 mmol) diethyl malonate and 60 ml ethanol (200 proof, freshly distilled with sodium). Into the solution was added 19.500 g (275 mmol) sodium ethoxide pre-dissolved in 120 ml ethanol (200proof, freshly distilled with sodium). The solution was then cooled to 0°C and stir for 20 minutes. Subsequently, 45.401 g (275 mmol) 1-bromohexane were added in to the solution dropwise. The mixture was then refluxed for 24 hours. Upon completion of reaction, the mixture was evaporated on a rotary evaporator under vacuum and the high boiling point liquid inside the flask was dissolved in distilled water. The water solution was then extracted by 150 ml hexane for 3 times. The organic phase was combined and evaporated to yield the crude product of diethyl 2,2-dihexylmalonate as an oil-like liquid which was directly used in the following synthetic step assuming 100% yield.

**2,2-dihexylmalonoic acid**
To the 500 ml round bottomed flask which contained the crude product of diethyl 2,2-dihexylmalonate were charged with 66.071 g (1000 mmol) potassium hydroxide, 150 ml of ethanol (95%) and 100 ml distilled water. The solution was then heated to 70°C for 20 hours. The mixture was later cooled to RT and acidified to pH = 2 with hydrochloric acid (1M). The solvent was removed by rotary evaporator under vacuum. The residue was extracted by 250 ml ethyl acetate for 4 times. The organic phase was combined and washed with brine, anhydrous magnesium sulfate. The solution was then filtered and evaporated on a rotary evaporator under vacuum. The resulting oil was wash with brine again and precipitated in cold hexane. The light yellow precipitate was recrystallized with the mixture of ethyl acetate and hexane. The relatively pure product which is white needle-like crystal was directly used in the next step of reaction without further purification. The yield was determined to be 17.976 g (52.9%, with respect to the starting material, diethyl malonate)

2-hexyloctanoic acid

To a 50 ml round bottomed flask was charged with 17.976 g of 2,2-dihexylmalonoic acid. Purged with Argon, the solid was heated to 170°C for 45 minutes. The product is a clear colorless liquid which weighed 14.325 g (95%) and was directly taken to the next step of reaction without further purification.

2-hexyloctan-1-ol

To a 500ml round bottomed flask were charged with 10.153 g (268 mmol) LiAlH₄ and 100 ml anhydrous THF. The solution was then cooled to 0°C. Under the protection of Argon, 14.325 g (62.83 mmol) 2-hexyloctanoic acid pre-dissolved in 100ml anhydrous THF was added dropwise into the solution. The reaction mixture was stirred at 0°C for another 4 hours and later quenched by adding 25 ml ethyl acetate. THF was removed by evaporation on a rotary
evaporator under reduced pressure. Subsequently, to the residue was added 25ml distilled water. The resulting gel was vigorously extracted by 125 ml ethyl acetate for 4 times. The organic phase was combined and washed with brine and dried over anhydrous magnesium sulfate. After filtration, the ethyl acetate solution was evaporated on a rotary evaporator under vacuum to yield a light yellow oil-like clear liquid. The alcohol could be easily purified by performing the column chromatography.

2-hexyloctanyl 4-methylbenzenesulfonate

The target compound was synthesized according to a literature procedure.23 A 50 ml round-bottomed flask was charged with 1.251 g (5.835 mmol) 2-hexyloctan-1-ol, 1.487 g (14.6 mmol) triethylamine, 0.085 g (0.88 mmol) trimethylamine hydrochloride and 6 ml dichloromethane. Then the mixture was cooled and stirred in an ice-water bath for 20 minutes. Afterwards, 1.354 g (7.00 mmol) 4-methylbenzenesulfonyl chloride was dissolved in 5 ml dichloromethane and the solution was added in a dropwise fashion into the reaction flask using a constant pressure funnel. Care was taken to maintain the temperature of the ice-water bath at 0°C during the reaction. The reaction progress was monitored by thin layer chromatography. The reaction was ended when 4-methylbenzenesulfonyl chloride was fully consumed and it took approximately 85 minutes. Upon the completion of reaction, 3.6 g (30 mmol) phosphoric acid and 5 ml water were added into the reaction mixture. The mixture was stirred for 15 minutes. Then the suspension was extracted with dichloromethane. The organic phase was later washed with brine, dried over anhydrous magnesium sulfate and evaporated on a rotary evaporator. The liquid residue was purified by silica column chromatography with chloroform as the eluent. The yield of 2-hexyloctanyl 4-methylbenzenesulfonate was calculated to be 1.302 g (61%), as a colorless liquid.
3,4,9,10-tetra-(2-hexyloctyloxycarbonyl) perylene

Into a 10 ml round-bottomed flask were added 0.133 g (0.333 mmol) 3,4,9,10-perylenetetracarboxyldianhydride, 0.639 g (1.332 mmol) tetrabutylammonium hydroxide (water solution, wt%: 55%), 4.5 ml DMSO and 4.5 ml acetone. The mixture was purged with nitrogen when it was heated at 40 °C for 4 hours. Subsequently, to the solution was added 0.65 g (1.766 mmol) 2-hexyloctanyl 4-methylbenzenesulfonate. The mixture was stirred at 40 °C for 60 hours. Then to the solution was added adequate amount of water to precipitate the desired product. Afterwards, water was removed by decantation. The solid precipitate was purified by column chromatography to yield 0.223 g (54%) of pure product as an orange solid.

Perylene-3,4-anhydride-9,10-di-(2-hexyloctyloxycarbonyl) (2)

Into a 50 ml round-bottomed flask we charged with 0.112 g (0.092 mmol) 3,4,9,10-tetra-(2-hexyloctyloxycarbonyl) perylene, 0.014 g (0.074 mmol) p-toluenesulfonic acid monohydrate and 1 ml n-octane. The mixture was then heated to 95 °C for 2 hours and 15 minutes. The reaction mixture was directly purified with column chromatography, yielding 2 0.028 g (38%) as a red solid.

Perylene-3,4-imide-9,10-di-(2-decyldodecyloxycarbonyl) (3)

Into a 10 ml round-bottomed flask were charged with 0.112 g (0.103 mmol) 1, 0.069 g (0.365 mmol) ammonium decanoate, 1.2g of imidazole and 0.5 ml toluene. Purged with nitrogen, the reaction mixture was heated at 130°C for 1 hour. The solution was then cooled down to 80°C and sufficient amount of water was added to dissolve imidazole. Subsequently, the suspension was extracted by 10 ml chloroform for 3 times. The organic phase was combined and washed with brine and dried over anhydrous magnesium sulfate. The chloroform solution was then concentrated on a rotary evaporator under reduced pressure. The crude product in concentrated
chloroform solution was purified through column chromatography, yielding 3 0.090 g (80%) as a red solid.

**Perylene-3,4-methyl-imide-9,10-di-(2-decyltetradecyloxy carbonyl)** (4)

Into a 10 ml round-bottomed flask were added 0.040 g (0.0369 mmol) 3, 0.016 g (0.0339 mmol) tetrabutylammonium hydroxide (water solution, wt%: 55%), 2.0 ml DMSO and 0.5 ml acetone. The mixture was purged with nitrogen when it was heated at RT for 1 hour. Subsequently, to the solution was added 0.021 g (0.148 mmol) methyl iodide. The mixture was stirred at RT for 30 minutes. Adequate amount of water was then added to the solution to precipitate the desired product. Afterwards, water was removed by decantation. The solid precipitate was purified by column chromatography to yield 4 0.021 g (52%) of pure product as an orange solid.

**$^1$H NMR** (CDCl$_3$, 600 MHz): $\delta$ (ppm) = 8.62 (d, $J = 7.98$ Hz, 2H, Ar), 8.48 (m, 4H, Ar), 8.10 (d, $J = 7.98$ Hz, 2H, Ar), 4.26 (d, $J= 6$ Hz, 4H, -OCH$_2$CH), 1.83 (m, 2H, CH), 1.46 – 1.19 (m, 80 H, CH$_2$), 0.85 (m, 12 H, CH$_3$).

**$^{13}$C NMR** (CDCl$_3$, 150 MHz): $\delta$ (ppm) = 168.07 (ester C=O), 160.30 (anhydride C=O), 137.59 (Ar), 133.56 (Ar), 132.93 (Ar), 131.86 (Ar), 131.39 (Ar), 130.16 (Ar), 129.30 (Ar), 126.38 (Ar), 123.49 (Ar), 122.04 (Ar), 117.94 (Ar), 68.69 (CO$_2$CH$_2$CH$_2$), 37.37 (CO$_2$CH$_2$CH), 31.95 (CH$_2$), 31.33 (CH$_2$), 30.02 (CH$_2$), 29.69 (CH$_2$), 29.39 (CH$_2$), 26.75 (CH$_2$), 22.69 (CH$_2$), 14.12 (CH$_3$)

**FT-IR (cm$^{-1}$):** 2925 (antisymmetric CH$_2$), 2854 (symmetric CH$_2$), 1766 (symmetric anhydride C=O), 1728 (antisymmetric anhydride C=O), 1710 (ester C=O), 1590 (aromatic ring stretch).

**HRMS (M+e):** calcd for C$_{72}$H$_{106}$NO$_7$ 1083.7967; found 1083.7886. MALDI with benzopyrene as the matrix.
2.6. References


13. The integration is shown in the Supporting Information.

14. Each branch in the branched flexible peripheral group can be considered as an \(n\)-alkyl chain.

15. More detailed discussion on the role of long alkyl peripheral chains can be found in the Supporting Information.


CHAPTER 3. NON-ORTHOGONALLY PACKED DISCOTIC LIQUID CRYSTALLINE PERYLENE DIESTER MONOIMIDES (PEI) WITH OLIGOMERIC ETHYLENE GLYCOL (OEG) SUBSTITUTION

3.1. Introduction

Perylene tetracarboxylic acid-based dyes are under intense investigations due to their promising applications. In particular, \(N, N'\)-disubstituted perylene tetracarboxylic diimides (PDIs) have been widely used as lightfast colorants,\(^{41}\) highly efficient fluorophores,\(^{42}\) the electron acceptor in solar cells,\(^{43}\) the active component in field effect transistors,\(^{44}\) liquid crystalline (LC) materials\(^{27,45}\) and versatile building block in self-assembly.\(^{46}\) Recently, perylene tetracarboxylic diester monoimides (PEIs), where an imide and two ester groups connect to the same perylene core, have also attracted considerable attention as more soluble alternative to PDIs.\(^{47}\) One of fields that witnesses a surging interest is organic photovoltaics, where perylene tetracarboxylic acid derivatives especially PDIs have been playing important roles as electron accepting and transporting materials. When being used as an electron acceptor, PEIs not only provide enhanced solubility over PDIs, but also offer an opportunity to tune the electron affinity of the acceptor to achieve the optimum energy conversion efficiency.

In order for a donor/acceptor organic photovoltaic system to achieve the optimal energy conversion efficiency, the electron affinity of the acceptor must be great enough to promote efficient exciton dissociation. On the other hand, an electron acceptor with an excessive electron affinity may lead to a deteriorated efficiency because of the reduced open-circuit voltage. In
other words, for a given electron donor, the best electron acceptor must have a matched electron affinity.\textsuperscript{48}

$N, N'$-disubstituted PDIs have their HOMO and LUMO orbital nodes at nitrogen atoms, thus the change of $N$-substitution has an insignificant effect on tuning the electron affinity of a PDI. Although modification on the carbocyclic scaffold (bay-area) leads to electronically tuned PDIs, such a functionalization results in the distortion of the originally planar perylene ring so that the $\pi$-stacking of PDI moieties becomes more difficult. When charge transport is concerned, planarity of PDI rings is preferred for establishing PDI $\pi$-stacks as efficient charge transport pathways.

The planarity of the perylene ring is expected to retain in PEIs when there are no bay-area substituents. Furthermore, PEIs are good organic electron acceptors with LUMO level at about 3.6 eV which is about 0.2 eV to 0.3 eV lower than that of PDIs.\textsuperscript{47a} Having the ability to use PEIs to replace the PDIs in those photovoltaic systems enable one to tune the electron accepting power of the acceptor for the best possible conversion efficiency, in addition to the substantially improved solubility in common organic solvents.

As candidates of charge transport materials, electronic wave function coupling between adjacent $\pi$-systems is one of key factors that substantially influences the intra-stack charge carrier transport. The electronic coupling is characterized by the transfer integral $J$ which describes the probability of a charge carrier moving from one molecule to its closest neighbors. The value of $J$ (or electronic coupling) is directly related to the intra-column $\pi$-stacking, i.e. the overlap of frontier orbitals. Such overlap is further related to the distance separating adjacent $\pi$-units and the azimuthal rotational angle which is shown in Figure 3.1.1.\textsuperscript{3} It has been revealed through theoretical calculation that in $\pi$-stacked PDI units multiple maxima and minima of $J^2$
exist as the angle changes from 0° to 90°. For electron transport, two maxima are at around 0° and 65°, while for hole transport, two maxima are at approximately 0° and 50°. Angles at around 30° and 90° for both electron and hole transport are corresponding with their $J^2$ minima. Due to the exceedingly large steric hindrance and electrostatic repulsive interaction, π-stacks with 0° rotation are not possible. In addition, with only two substitution sites for the attachment of flexible side chains, a 90° rotation angle between adjacent intra-stack PDI units is the most preferred as required by space filling. Unfortunately, frontier orbital overlap at such an angle supports the efficient transport of neither holes nor electrons. Clearly, the rotation angle is one crucial parameter to be optimized especially when materials are designed as candidates of n-type semiconductors.

Figure 3.1.1. Azimuthal rotational angle showing with two adjacently stacked PDI molecules.

In addition to the electronic characteristics at the molecular level, the hierarchical structure of perylene derivatives in the solid state has a pronounced effect in their device performance. For enhanced exciton diffusion length and charge carrier mobility, it is imperative to improve the solid-state supramolecular organization. Inducing LC order is one effective way of doing so. As the perfect combination of molecular mobility and order, liquid crystals feature the ability of self-healing, self-organization as well as responding to external stimuli. While
there are numerous reports on LC PDIs\textsuperscript{27, 45} and perylene tetracarboxylic esters,\textsuperscript{41b} LC order in PEIs has only been reported once, to the best our knowledge.

Both smectic\textsuperscript{45a, 45d-f} and columnar\textsuperscript{27, 45b, 45c} LC PDIs have been reported. In a smectic phase, the rigid PDI cores are microphase-segregated from flexible tails forming an alternating rigid-flexible layered structure. Typically the intra-layer organization of PDI moieties is of short-range order. However, we have observed 2D crystalline order of PDI cores in a highly ordered smectic LC PDI.\textsuperscript{45a} In columnar phases, the rigid PDI cores are also microphase-segregated from flexible tails. However, instead of forming layers, they stack on top of each other forming supramolecular columns. These columns further self-assemble into 2D ordered lattices. The fact that PDIs can form both smectic and columnar phases can be considered as the natural consequence of fulfilling the space-filling requirements. Most of PDIs that exhibit smectic LC phases have only two flexible tail attached. In contrast, those column-forming PDIs typically possess six flexible tails, although it has been reported recently that PDIs with four flexible tails can also self-assemble into a columnar LC phase when highly flexible oligomeric ethylene glycol chains are used.\textsuperscript{27} The common structural element that has been observed in all LC PDIs is the PDI $\pi$-stack due to strong $\pi$-$\pi$ interaction between adjacent PDI units. In a smectic phase, such $\pi$-stacking interaction is a part of driving force that leads to the formation of layered structures. However, when a large number of flexible tails (for instance, six) are connected to a PDI core, the smectic phase becomes not accessible because it is impossible for rigid cores to fill the space while the flexible tails segregate into micro-regions with a reasonable density. As the consequence, supramolecular columns that consist of $\pi$-stacked PDI molecules form instead. Discotic columnar LC phases have also been observed in perylene tetracarboxylic esters, where four alkyl chains are connected to the perylene core via ester linkages.\textsuperscript{21a}
To encourage the appearance of LC phases in PEIs, efforts should be made to lower the free energy of the target LC phase with respect to the corresponding crystalline phase. This can be done by either enhancing the stability of the LC phase or reducing the stability of the crystalline phase, or doing both. If a crystallization process is kinetically hindered, the LC phase could be observed during cooling, even if the clearing point of the LC phase is lower than the melting point of the crystalline phase so that the LC phase cannot be observed after the melting of the crystalline phase. Such a LC phase is a monotropic phase. Since there are at least three flexible tails attached to a PEI core, it is hard to imagine that a PEI can self-assemble into a smectic phase when the space filling is considered. Therefore we expect that only columnar LC phases could be developed in PEIs.

3.2. Molecular design

Mesogens which can be easily engineered into DCLC phase share many structural characteristics in common. Those properties include: 1. Disc shaped molecules; 2. Symmetrical substitution; 3. No less than four substituents; 4. Strong $\pi$-$\pi$ interaction. However, with the general molecular structure shown in Figure 3.2.1, PEIs have only three substitution sites located geometrically in an asymmetrical manner. From the single molecular perspective, chain density is much lower near the imide part of the mesogen. However, upon aggregation and formation of the DCLC phase, every molecule could rotate along its plane normal and the empty space could also be filled with side chains coming from molecules of adjacent layers. Thus, the chain density could be averaged and uniform even when the DCLC phase is originated from asymmetrical mesogens like PEIs.

![Molecular structure of PEI](image)
Figure 3.2.1. Molecular structure of perylene tetracarboxylic diester monoimides (PEIs)

To study the phase behavior of PEI derivatives, we have designed and synthesized three different series of compounds. Alkyl chains have been the most commonly used substituents for their advantages in availability, chemical stability, good synthetic accessibility and hydrophobicity. Effort has been made on the investigation of liquid crystallinity of perylene tetracarboxylic tetraester (PTE) compounds with the general structure shown in Figure 3.2.2. DCLC phases have been identified with compounds conceiving linear alkyl substituents that have chain length ranging from two to nine carbons.\textsuperscript{21a} To make rational design of molecular structures, the formation of LC phase must be reviewed from an energy perspective. The free energy is affected by both entropy and enthalpy of the system. Enthalpy is a reflection of the overall interactions in a system. It is energetically beneficial to have enthalpy decrease as the total free energy will be lowered. The reduction of enthalpy is related with a process of increasing order as highly ordered system optimizes the inter-molecular interactions. For instance, crystallization of flexible chains is an enthalpy driven process which is affected by the inter-chain interactions as well as interactions between soft chains and rigid cores. On the other hand, the total free energy could be lowered by increasing the entropy of a system, which is associated with the decrease in order. The entropy contribution is magnified by the increasing of temperature. When a system is in an isotropic state, entropy is the dominant factor to the free energy minimization. As the intermediate state of matter which is between the ordered crystal and the isotropic liquid, LC materials feature coexistence of enthalpy and entropy dominant moieties in the same molecule. When the entropy contribution due to side chain melting is substantial enough to compensate for the enthalpy change from both aromatic cores and tails
(order of aromatic core packing is usually found to be higher in the crystalline sample compared with the LC one), molecules could self-assemble into columns (one of possible LC phases) which could further arrange themselves into a 2D lattice.

\[
\begin{align*}
R &= \text{C}_n\text{H}_{2n+1}, n = 2, 3, 4, 5, 6, 7, 8, 9, 10
\end{align*}
\]

**Figure 3.2.2.** Molecular structure of 3,4,9,10-tetra-(n-alkoxycarbonyl)-perlenes

As our molecular design has a specific requirement of forming DCLC phase, it is important to consider the volume ratio between the core and side chains as well as the collective cross-sectional area of side chains. While the three chain configuration of PEIs tends to lead to a DCLC phase, collective cross-sectional area of side chains may not be enough to support a DCLC phase. The LC phase will lose its thermotropic stability when the melting point of the underlying crystalline phase is higher than the clearing point of the LC phase, resulting in crystalline or monotropic LC material.

PEIs as mesogen have bigger core size compared to that from PTEs as the imide ring is rigid and coplanar to the perylene core while the ester groups are somewhat flexible and not coplanar to the aromatic part. Moreover, fewer substitution sites are available for incorporating flexible side chains. Therefore, it is intuitive to think that higher volume of side chains are required to cover the surface of the relatively bigger column in the LC phase as well as to provide larger entropy increase. If taking total number of carbons in the side chains of PTE compound as the rough reflection of the total chain volume, the range that gives rise to the LC phase is from 8 to 40. Thus, for the first series, we chose to synthesize three compounds (Figure 3.2.3) with octyl, decyl and dodecyl groups (the range of the number of carbons is from 24 to 36).
as they seem empirically reasonable to support a DCLC phase with PEI cores.

![Molecular structure](image1)

**1a**: \( R=-(CH_2)_8H \)  
**1b**: \( R=-(CH_2)_{10}H \)  
**1c**: \( R=-(CH_2)_{12}H \)

**Figure 3.2.3.** Molecular structures of three compounds from series 1

The linear architecture of side chains used in the first series easily allows parallel packing of all anti-conformed alkyl groups, which leads to the crystallization. As learned from the melting points of linear alkanes, the odd-even effect shows that less efficient packing of molecules may reduce the order and decrease the crystallization tendency. Therefore, for the second series, we incorporated the 3,7-dimethyloctyl group (structure shown in Figure 3.2.4). With two methyl groups on the main chain, it is expected that the alkyl groups will have difficulty to take highly ordered packing. As the tail shares the same number of carbons with \( n \)-decyl group, it provides an opportunity to observe the influence by the introduction of branches and to better understand the competitive nature of side chain isotropization against crystallization.

![Molecular structure](image2)

**Figure 3.2.4.** Molecular structure of compound 2a from series 2

The alkyl chains are considered to be not flexible enough as gauche-conformers are at
higher energy state compared to anti-conformers. Thus, those more coil-like alkyl groups as required by space filling are energetically disfavored. Moreover, the branched alkyl group is even more rigid due to the extra steric hindrance originated from two methyl groups. In order to increase the cross-sectional area and the space filling capability of substituents, we designed the third series of compounds with OEG moieties as substituents. We have chosen the OEG for two reasons. First, OEG is known as materials with a lower melting point due to the higher conformational flexibility comparing with the alkyl counterparts. The oxygen atom bears lower rotational energy barrier compared to the carbon atom in a methylene group. It is expected that the more liquid-like tails would lead to DCLC phases with better stability and lower clearing points. Second, ethylene glycol groups could largely increase the solubility of PEI derivatives in a variety of organic as well as inorganic solvents. It is of our interest to see if OEG substituted PEIs could give rise to water soluble supramolecular polymers. Such system may combine properties from conventional polymeric material such as mechanical strength with those arise from the supramolecular self-assembly, such as reversibility and responsiveness to external stimulus.\textsuperscript{50} As depicted in Figure 3.2.5, we systematically decreased the number of repeating units in polyethylene glycol groups. As the chain becomes shorter, it is expected that the clearing point will increase, leading to a wider range of operational temperature which is desirable in the application. At the same time, the decrease of side chain volume increases the overall percentage of the aromatic core, which is the electronically active component of the material, leading to a higher atomic efficiency (the ratio of number of atoms from the functional moiety to the number of atoms from the entire molecule) and better electronic performance per unit weight.
The design of the fourth series was to help understanding the influence of chemically asymmetrical substitution on the liquid crystals’ phase behavior (Figure 3.2.6). The difference in the chain length may lead to difficulty in highly ordered packing and further reduce the stability of the crystalline phase. Therefore, thermal properties of the LC phase may be tuned (e.g. changing phase transition temperatures). Furthermore, it is interesting to see if the rotation angle is sensitive to the spatially uneven chain volume distribution on a molecule.

**Figure 3.2.6.** Molecular structure of compounds from series 4

### 3.3. Thermal properties and phase behaviors

No LC phase can be identified with any compound from series 1. In a typical LC phase, π-stack and side chains show different degree of decrease in order. In contrast to the strongly
interacted rigid parts, soft tails are melted into a state that is almost isotropic. Upon further increase of temperature, the relatively ordered part, $\pi$-stacks, will eventually undergo the same isotropization process, contributing to the total free energy change. Because of the overall low degree of order, for the same compound, the free energy of the LC phase is close to that of the isotropic phase. Thus, phase transition corresponding with the isotropization of the entire molecule should correspond with a relatively small enthalpy and entropy change. It is common among DCLC compounds that transitions from LC to isotropic liquid exhibit enthalpy changes of only a few kJ/mol. DSC traces for compound 1a, 1b and 1c are shown in Figure 3.3.1. Important thermodynamic parameters are summarized in Table 3.1. The crystalline nature was revealed by large enthalpy changes at phase transitions and large undercooling when compounds enter an ordered state from the isotropic state. For all three compounds, two phase transitions with endothermic peak upon heating were observed. Two crystalline phases noted as Cr1 and Cr2 were assigned to phases before and after the first transition, respectively. This assignment is based on large enthalpy values found with final isotropization for every compound. It agrees with the general finding that the clearing point decreases while chain length increases. However, no LC phases could be obtained during either heating or cooling process.
Figure 3.3.1. DSC traces of compound 1a, 1b and 1c with ramp rate at 20 °C/min. Samples were heated to isotropic state before measurements to eliminate thermal history.

Table 3.3.1. Summary of important thermodynamic parameters of series 1 compounds

<table>
<thead>
<tr>
<th>Compounds</th>
<th>PHASE BEFORE [Phase transition temperature(onset, °C)] (enthalpy(kJ/mol)/entropy (J/mol•K))</th>
<th>PHASE AFTER*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>Cr\textsubscript{1} [33.7] (10.7/34.7) Cr\textsubscript{2} [168.5] (29.5/66.8) Iso</td>
<td></td>
</tr>
<tr>
<td>1b</td>
<td>Cr\textsubscript{1} [70.5] (23.0/66.9) Cr\textsubscript{2} [154.4] (29.1/68.2) Iso</td>
<td></td>
</tr>
<tr>
<td>1c</td>
<td>Cr\textsubscript{1} [90.8] (28.1/77.1) Cr\textsubscript{2} [144.7] (31.2/74.6) Iso</td>
<td></td>
</tr>
</tbody>
</table>

* measured with ramp rate at 20 °C/min

* Cr\textsubscript{1}: crystalline phase 1; Cr\textsubscript{2}: crystalline phase 2; Iso: isotropic phase
The crystalline phase assignment is confirmed by 1-D integration of XRD patterns which are summarized in Figure 3.3.2. XRD data were collected from powder samples at temperature in between two phase transitions. Compounds were heated to isotropic liquid followed by cooling down to the desired temperature. Multiple sharp diffractions were registered in the 2θ angle range from 15 ° to 25 ° (weak diffractions are magnified and shown in the inset), suggesting the crystallized linear alkyl side chains. Similar characteristics have been identified with RT 1-D XRD, suggesting different crystalline phases.

![Figure 3.3.2](image)

**Figure 3.3.2.** 1-D integration of XRD patterns collected at 130 °C, 100 °C and 100 °C with 1a, 1b and 1c, respectively. Compounds were heated to isotropic state before measurement to eliminate thermal history. Inset shows weak diffraction peaks at wide angle.
Polarized light microscopic (PLM) pictures shown in Figure 3.3.3 are lacking typical textures commonly seen with LC phases. Instead, RT pictures revealed a cracked texture for all compounds which indicates the lacking of molecular mobility. All compounds are difficult to align on glass surface by applying mechanical shearing force. No obvious difference was observed between phases of Cr₁ and Cr₂. Therefore, the PLM results also support the idea that none of compounds from series 1 possesses a LC phase above RT.

Figure 3.3.3. Polarized optical microscopic pictures taken with orthogonally aligned polarizers. Samples were melted into isotropic liquid state followed by cooling down to RT at a rate of 20 °C/min. Scale bars in pictures mark 100 μm. (a), (c) and (e) were pictured at RT with compound 1c, 1b, and 1a, respectively. (b), (d) and (f) were pictured at 100 °C, 100 °C and 130 °C with compound 1c, 1b, and 1a, respectively.

All three compounds experience one phase transition before being heated to the isotropic
It is assigned as a crystalline to crystalline phase change as evidenced by DSC, XRD and PLM studies. However, it is of our interest to unveil more detailed information about what properties have been undergoing changes as the newer phase appears. It may help us understanding why our compounds in series 1 failed to enter the LC phase after their first phase transitions. To answer those questions, temperature dependent FT-IR measurements with compound 1c were done in order to monitor the side chain conformational change. As shown in Figure 3.3.4, IR absorption peaks corresponding with symmetrical and asymmetrical C-H bond stretching were plotted against the temperature. As revealed by theoretical calculation, C-H vibrational frequency increases as the percentage of gauche-conformation in alkyl side chains becomes greater. In Figure 3.3.4, the abrupt increase in vibrational frequency for both absorption bands at around 89 °C clearly corresponds with the first phase transition temperature registered on the DSC heating curve (it should be noted here that due to the time spent to collect data points, the actual heating rate during IR experiment was much lower than 20 °C/min as employed in DSC measurements, which explains the relatively low transition temperature), indicating a sudden increase of gauche-conformers in alkyl side chains. However, the absorption frequencies for both vibrational modes are still much lower compared with that of the compound’s isotropic state, to which the transition happens at around 137 °C. Therefore, as supported by 1D XRD data, we could conclude that despite of the change of conformation at the first phase transition, the linear alkyl part of compound 1c is still too rigid to melt into a LC phase. From the energetic perspective, the potential entropy increase associated with increased number of gauche-conformers in melted state does not compensate for the unfavorable enthalpy change. To solve the problem that prevents side chains from melting, two solutions were proposed. First, increase the steric hindrance of side chains so that the ordered packing becomes much more difficult for
all anti-conformers (design of series 2). This could lead to a decreased stability of the crystalline state. Second, reduce the free energy of gauche-conformers by lowering the rotation energy barrier of C-C bond so that the side chains are able to make greater contribution to entropy increase while less affected by the steric hindrance (design of series 3).

![Graphs](a) and (b) showing vibrational frequency changes of compound 1c with increasing temperature probed by FT-IR. More data points were taken when temperature is near phase transition. (a) Symmetrical C-H bond vibration. (b) Asymmetrical C-H bond vibration. Samples were heated to isotropic state before measurements to eliminate thermal history.

To realize the first solution, we designed the only compound 2a as series 2. Two methyl groups are substituted on the octyl main chain, creating a chiral center near the perylene core. 1-bromo-3,7-dimethyloctane was received and used as racemic compound. Thus, it is expected that side chain packing would be more difficult than its linear counterpart even when the overall number of anti-conformers stay the same. DSC traces and PLM picture are shown in Figure 3.3.5. Only one phase transition could be observed by DSC, indicating a different phase behavior of 2a due to the structural change compared to the similar phase behaviors shared by
compounds from the first series. However, enthalpy change is still large enough to assume a crystalline phase below the clearing point. Both enthalpy and entropy changes are much smaller compare to compound 1b (sum of two transitions) which has the same number of carbons in the side chains. This may be an indication that branched 3,7-dimethyloctyl side chains are taking a high free energy packing mode as they crystallize. The smaller entropy change indicates that the branched octyl group is less conformational flexible compared to the linear decyl group in the isotropic liquid state. This is easily understandable as rotation of C-C bond could be more sterically hindered by methyl substituents (gauche-conformation with even higher energy level). Therefore, as side chains of compound 2a, 3,7-dimethyloctyl group does not support the formation of DCLC phase as it is less efficient in filling up the space around a supramolecular PEI column, especially when only three chains per PEI molecule are available.

![DSC heating and cooling curves of compound 2a with a ramp rate at 20 °C/min](image)

![Polarized optical microscopic picture taken at RT, Sample was melted into isotropic liquid state followed by cooling down to RT at a rate of 20 °C/min. Scale bar in the picture marks the length of 100 μm. Samples were heated to isotropic state before measurements to eliminate](image)

**Figure 3.3.5.** (a) DSC heating and cooling curves of compound 2a with a ramp rate at 20 °C/min (b) Polarized optical microscopic picture taken at RT, Sample was melted into isotropic liquid state followed by cooling down to RT at a rate of 20 °C/min. Scale bar in the picture marks the length of 100 μm. Samples were heated to isotropic state before measurements to eliminate
thermal history.

The crystalline nature of 2a was also verified by 1-D XRD as shown in Figure 3.3.6. Multiple sharp peaks could be found in the region from $10^\circ$ to $30^\circ$, corresponding with crystallized side chains.

![Figure 3.3.6. 1-D integration of XRD pattern of compound 2a collected at RT. Compounds were heated to isotropic state before measurement to eliminate thermal history Inset shows weak diffraction peaks at wide angle.](image)

As the next step of the effort to induce a DCLC phase in PEIs, OEG chains were attached to the PEI core. The population of anti- and gauche- conformers are closely related to their energy levels. Oxygen atoms provide the entire chain with a higher freedom (much lower energy barrier) of bond rotation as oxygen is not substituted with any atoms.

To systematically study the properties of OEG substituted PEIs, we designed three
compounds, 3a, 3b and 3c, with increasing number of -(CH_2CH_2-O)- repeating units. DSC result and PLM picture of compound 3a were shown in Figure 3.3.7. There is only one transition on either heating or cooling trace in the DSC experiment. The large enthalpy change value and lacking of typical LC texture under the polarized optical microscope suggested that 3a melts into isotropic liquid state directly from a crystalline phase. 1-D XRD in Figure 3.3.8 confirmed the crystallinity of 3a’s solid phase by showing multiple sharp diffractions at the side chain crystallizing region. In this case, we concluded that OEG units in 3a are too short to make sufficient entropy contribution to the formation of the LC phase.

![DSC heating and cooling curves of 3a](image1)

**Figure 3.3.7.** (a) DSC heating and cooling curves of 3a with a ramp rate at 10 °C/min (b) Polarized optical microscopic picture taken at RT, Sample was melted into isotropic liquid state followed by cooling down to RT at a rate of 10 °C/min. Scale bar in the picture marks the length of 100 μm. Samples were heated to isotropic state before measurements to eliminate thermal history.
Figure 3.3.8. 1-D integration of XRD pattern of compound 3a collected at RT. Sample was heated to isotropic state before measurements to eliminate thermal history.

DSC results and PLM pictures of compound 3b and 3c were shown in Figure 3.3.9. Important thermodynamic parameters are summarized in Table 3.3.2. For both compounds, only second heating and the first cooling curves are shown in the graph. The first heating in the DSC measurement was used to eliminate any thermal history of tested samples. Under polarized light microscope, sample of compound 3b melted into an optically isotropic liquid at around 70 °C. Such phase transition is corresponding with the first exothermic peak in the DSC heating trace shown in Figure 3.3.9a. The peak is associated with an enthalpy change of 2.8 kJ/mol, suggesting a LC phase below this phase transition temperature. The phase assignment is also supported by the small undercooling which is within only a few degrees when cooling down from liquid at a much lower ramp rate. The second exothermic peak at relatively higher
temperature (around 107 °C) is due to small amount of crystallization of the sample during cooling and subsequent heating process, which will be explored and explained in detail later. Similar conclusion could be made to compound 3c due to similar thermodynamic behaviors revealed by DSC and PLM. Sample of 3c melted into dark flowing liquid under crossed polarizers at about 35 °C, which is corresponding with the only exothermic peak that could be observed on DSC heating curve when a heating rate of 10 °C/min is adopted (Figure 3.3.9b). Undercooling for compound 3c is within a few degrees upon slow cooling rate as well. PLM pictures in Figure 3.3.9c and Figure 3.3.9b can be obtained when samples are slowly cooling down from isotropic state and annealing at temperatures close to phase transitions for about 30 minutes to 1 hour. Textures are showing dendritic growth for both compound 3b and 3c, which indicate the development of a DCLC phase. It is worthwhile to mention that the picture in Figure 3.3.9d was taken with slightly uncrossed polarizers. The area is essentially dark under orthogonally crossed polarizers. This observation suggests a homeotropic alignment where column axes are all aligned to be perpendicular to the substrate.
Figure 3.3.9. (a) DSC heating and cooling curves of 3b with a ramp rate at 20 °C/min (b) DSC heating and cooling curves of 3c with a ramp rate at 10 °C/min (c) and (d) Polarized optical microscopic pictures of 3b and 3c, respectively, taken at temperature closely below phase transition upon cooling. Samples were melted into isotropic liquid state followed by cooling down to proper temperature at a rate of approximately 0.05 °C/min. Annealing is required to obtain pure textures. Slow cooling rate is applied in order to improve the alignment. Picture in (d) was taken with polarizers slightly uncrossed. It was otherwise dark. Scale bars in the picture mark the length of 100 μm.

Table.3.3.2. Summary of important thermodynamic parameters of series 3 compounds

<table>
<thead>
<tr>
<th>Compounds</th>
<th>PHASE BEFORE [Phase transition temperature(°C)]$^\text{5}$ (enthalpy(KJ/mol)/entropy (J/mol*K))</th>
<th>PHASE AFTER$^*$</th>
</tr>
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<tbody>
<tr>
<td>3a</td>
<td>Cr <a href="45.2/99.7">179.8</a> Iso</td>
<td></td>
</tr>
<tr>
<td>3b</td>
<td>Colh <a href="2.8/8.1">70.3</a>$^5$ Iso</td>
<td></td>
</tr>
<tr>
<td>3c</td>
<td>Colh<a href="1.4/4.5">35.4</a> Iso</td>
<td></td>
</tr>
</tbody>
</table>

$^5$ Samples 3a and 3c were measured with ramp rate at 10 °C/min, sample 3b was measured with ramp rate at 20 °C/min to avoid crystallization
1-D XRD patterns of powder sample 3b and 3c are shown in Figure 3.3.10. Different from crystalline compounds 1a-c and 2a, there are only two sharp diffractions at wide angle which are corresponding to $\pi$-stacking of aromatic cores of PEI molecules and Si powder as the internal standard. The otherwise broad and smooth scattering suggested an isotropically melted state of side chains. On the other hand, the existence of sharp small-angle diffractions testified the ordered nature of the phase. Therefore, LC phases with compound 3b and 3c were identified. Furthermore, a 2D hexagonal lattice of supramolecular columns has been suggested based on the d-spacing ratio between each small angle diffraction peak and the first diffraction peak which has the smallest $q$ value (which is assigned as (10)). Those weak small angle diffractions were indexed as (11), (20) and (21) for compound 3b and (11) and (20) for compound 3c, based on the suggested 2-D lattice (Figure 3.3.11). Cell parameters were calculated and summarized in Table 3.3.3. While two compounds share similar $\pi$-stacking spacing, inter-column distance is 1.73 nm for compound 3b and 1.92 nm for compound 3c. The difference d-spacing reflects the dependence of the column size on the length of OEG side chains.
Figure 3.3.10. (a) and (b) are 1D XRD patterns of 3b and 3c at RT with small-angle diffractions indexed, respectively. Insets show the weak small-angle diffractions. The peak marked “Si” corresponds to the diffraction from crystalline silicon powder that were added as the calibration standard. Samples were heated to isotropic state before measurements to eliminate thermal
history.

Figure 3.3.11. Schematic drawing of 2D hexagonal lattice of supramolecular columns

Table 3.3.3. Cell parameters of DCLC phase of 3b and 3c

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$\alpha$ ($\beta = \gamma = 90^\circ$)</th>
<th>$a=b$</th>
<th>$c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3b</td>
<td>60 $^\circ$</td>
<td>1.73 nm</td>
<td>0.346 nm</td>
</tr>
<tr>
<td>3c</td>
<td>60 $^\circ$</td>
<td>1.92 nm</td>
<td>0.345 nm</td>
</tr>
</tbody>
</table>

XRD analysis is based on assumptions of a hexagonal 2D lattice, the scale of the structural element and molecular orientations. It is safely assumed that the 2D packing of supramolecular columns is happening on a nanometer scale while intra-column $\pi$-stacking spacing is much smaller. Therefore, diffractions appeared in small and wide angle regions could be well separated and provide information to solve each structural element. As a complement, polarized IR (PIR) is an approach that directly probes the molecular orientation. The rigid part of the PEI molecule exhibits three characteristic vibrational absorption bands on IR spectra, two of which come from the symmetrical and asymmetrical stretching of the imide carbonyl group,
while the other comes from the out of plane bending of C-H bond on the perylene ring. As shown in Figure 3.3.12, the transition moment of three vibration modes are in three directions that are orthogonally related.

Figure 3.3.12. Dipole moment changes due to bond vibrations in a PEI molecule, directions of changes are indicated by arrows

A vibration mode absorbs in the IR range when two major conditions are met. First, the frequency of the incident IR light should match the energy difference between two vibrational energy levels (usually the one between the vibrational first excited state and ground state) of the mode. Second, for this resonance oscillation to happen, the electric field vectors of the incident light and the transition moment direction of the bond must be non-orthogonal and the maximum absorption occurs when they are parallel. In practice, the IR incident beam is a continuous spectrum that covers a wide range of frequencies. The electric field vectors can be easily regulated by a linear polarizer. At the molecular level, three abovementioned bond vibrational
modes feature different transition energies and transition moment directions with respect to the perylene ring plane. As depicted in Figure 3.3.13a, they construct a 3D Cartesian coordinates with the perylene ring overlapping the x-y plane. Oriented samples could be obtained by applying a thin layer of the material on the KBr salt plate followed by mechanical shearing. Because molecules are highly aligned (which could be examined through PLM observation), transition moments fit in a Cartesian coordinates at the macroscopic level throughout the entire sample. Therefore, it is expected that changes of absorption intensities could be observed as the polarizer rotates from 0 ° to 90 °. Based on no assumptions, the relationship between such changes and polarizer angles is a direct reflection of the molecular orientation.

![Figure 3.3.13](image-url)

**Figure 3.3.13.** (a) Molecular coordinate (purple: asymmetric stretching; red: symmetric stretching; green: C-H out of plane bending). (b) Electric field vectors of linear polarized IR incident beam and their relation to the sample substrate and the shearing direction.

In experiments, 3b and 3c were melted before being applied on the KBr IR pallets in order to remove thermal history. Samples were further sheared mechanically and placed in the sample holder with the direction shown in Figure 3.3.13b. Polarized IR spectra were collected with two polarizing directions at 0 ° and 90 ° (directions shown in Figure 3.3.13b). Spectra are
displayed in Figure 3.3.14. Large dichroism ratios (about 7~10) have been observed which suggests that molecules are well aligned. The strongest absorptions from two types of carbonyl stretching were observed with polarizer setting at 0° while the absorption from C-H vibration is found to be the most intense at 90°. Therefore, we concluded that the molecular plane which encompasses imide carbonyl transition moments is horizontal (0°) and thus perpendicular to the KBr substrate.

**Figure 3.3.14.** (a) PIR spectrum of 3b showing carbonyl stretching. (b) PIR spectrum of 3b showing C-H bending. (c) PIR spectrum of 3c showing carbonyl stretching. (d) PIR spectrum of 3c showing C-H bending.
Solid and solution UV spectra are shown in Figure 3.3.15. The difference between the solution and solid UV is due to the extended aggregation through $\pi-\pi$ stacking. The spectra of the dilute chloroform solution originate from the absorption of unassociated single molecules, which peak at 506 nm. In contrast, the solid UV spectra are significantly different from their corresponding dilute solution counterparts, indicating the formation of PEI $\pi$ stacks, which changes HOMO and/or LUMO energy levels due to strong intermolecular $\pi$ orbital overlap.

**Figure 3.3.15.** (a) RT UV of 3b in diluted chloroform solution ($4.721 \times 10^{-6}$ M). (b) RT UV of solid 3b coated on quartz glass, sample was melted before measurement in order to remove
thermal history (c) RT UV of 3c in diluted chloroform solution \(2.843 \times 10^{-6}\) M) (d) RT UV of solid 3c coated on quartz glass, sample was melted before measurement in order to remove thermal history.

3.4. In-depth structural analysis and intra-column molecular packing resolved by 2D XRD

1-D integration of XRD pattern from powder samples separates intra-column from inter-column structures according to wide or small 2θ angles of diffractions. However, this classification principle does not work when more than one diffraction share the same diffraction angle. For example, a higher order diffraction originates from a large structure may share a similar 2θ angle with the first order diffractions of a smaller scaled structure. Moreover, intra-columnar molecular packing may sometimes involve a helical rotation which repeats the starting position every few layers. The diffractions from such rotated packing could have relatively small 2θ angles depending upon the nature of the helice. Therefore, 1D XRD depicts only the periodicity information of the molecular assembly. On the other hand, material design requires understanding of detailed structural information to enable the engineering at the molecular level. The DCLC phase facilitates charge carrier hopping within the \(\pi\)-stacked columns as the charge carrier mobility is several hundred times larger than that of the other two dimensions. Having the ability to draw exact picture of molecular assembly is crucial to relate the intra-columnar packing to the charge transport property of the material. Therefore, 2-D XRD experiments on fiber LC samples were carried out. The technique allows separation of diffractions not only based on 2θ angles, but also directions along which electron density varies. Combining with force field simulations, information such as rotation angle could be obtained. For the sake of comparison, Figure 3.4.1 summarizes both powder and aligned 2D XRD patterns collected from
Figure 3.4.1. (a) Powder 2-D XRD pattern of 3b at RT (b) Powder 2-D XRD pattern of 3c at RT (c) Aligned 2-D XRD pattern of 3b at RT (d) Aligned 2-D XRD pattern of 3c at RT. Samples were melted into isotropic liquid before mechanical shearing in order to remove thermal history. For (c) and (d), shearing direction is pointing up. Arrow in the middle indicates the shearing direction.
Diffractions from (10), (11), (20), (21) planes of 2-D hexagonal lattice are all positioned on the equatorial axis. The strong $\pi$-stacking diffraction at wide angle is concentrated as an arc and peaks the intensity on the meridional axis. These observations agree with the PIR analysis of the molecular orientation and further confirmed the Col$_h$ mesophase assignment. In a DCLC phase, $\pi$-stacks align uniaxially along the direction of the mechanical shearing force. Therefore, diffractions originated from the 2-D column arrangement are spread horizontally on the equatorial axis. On the other hand, electron density varies along the direction of columnar axis as the result of intra-column $\pi$-stacking of PEI cores. Thus, the diffraction arises from $\pi$-stacking can only be observed along meridional axis. Diffused diffractions and scatterings are also important as they contain information about side chain arrangement and intra-column molecular packing. First, it should be noted that the only diffraction on the meridional direction reflects the $\pi$-stacking order. Absence of diffraction splitting (splitting results into two separated diffractions with two intensity maxima locating symmetrically about the meridional axis) indicates that the plane of discotic mesogen is perpendicular to the column axis. Second, the diffused diffractions on the quadrants are originated from intra-column inter-mesogen periodicity beyond simply $\pi$-stacking. The fact all those diffractions are very diffuse implies that those periodicity is of short-range and thus the 3D crystalline order does not exist. Moreover, the diffused scatterings in the range of 1.3~1.7 Å$^{-1}$ form a halo with nearly uniform intensity distribution over 360°. This has suggested a non-orientated side chain packing despite a highly oriented column packing, which should be attributed to their liquid-like characteristic. Taking compound 3b as the example, the d-spacing relationship between diffused diffractions and the $\pi$-stacking order is revealed in Figure 3.4.2. Four quadrant diffractions’ projections on the meridional axis have the d-spacing exactly 3 times as the inter-molecular distance of the $\pi$-stack,
suggesting a 3-1 helical rotation within the column.

![Figure 3.4.2. Calculated d-spacing distances from intra-column \(\pi\)-stack and diffused diffractions at quadrants. 2-D XRD pattern obtained with a sheared sample of 3b in DCLC phase at RT. Shearing direction is pointing up as marked by the arrow.]

To verify the proposed intra-column structure, the simulated 2-D XRD pattern has been generated by molecular dynamics calculations (shown in Figure 3.4.4) in order to compare with the experimental one. The single column packing model used for calculation is shown in Figure 3.4.3. Within the column, PEI mesogen rotates towards the same direction with a 120° rotational angle with respect to the mesogen from one layer below. This setting is based on the preliminary d-spacing calculation of four quadrants diffractions. It should be noted that the 2D lattice of column packing is not calculated and all diffractions on the equator of the simulated pattern
should not be considered when comparing with the real pattern. Also, instead of the exact molecule of 3b and 3c, structures used in the simulation were modified. The OEG tails are substituted by a much simpler methyl group (molecular structure is shown in Figure 3.4.3). This replacement is based on two reasons. First, the substitutions are not completely removed as they play important role in aggregation. The methyl group simulates the steric hindrance that the OEG tail would cause in the intra-columnar molecular packing. It is assumed that methylene groups at close periphery of PEI mesogen contribute to most of steric hindrance due to the substitution. Second, with simple groups, the model structure spares the heavy calculation duty due to large number of atoms in an OEG tail.
Figure 3.4.3. (a) Structure of the PEI molecule used in the simulation. (b) Single column of PEI molecules that gives rise to the simulated 2D XRD diffraction fiber pattern as shown in Figure 3.4.2.

Figure 3.4.4. Calculated 2D XRD pattern by simulation (on the left) in comparison with real 2D XRD pattern from Figure 3.4.2

The good qualitative match between the simulated and the real pattern supported the proposed model. The schematic drawing showing the top view of energy minimized packing mode is depicted in Figure 3.4.5.
To summarize the LC phase structure, molecules aggregate into column-like structures through $\pi$-$\pi$ interactions. Intra-column packing is highly ordered while the OEG tails are melted into a liquid-like state as evidenced by DSC and XRD. The OEG substituents are conformationally soft to support a DCLC phase. A 120° rotation angle is determined and is associated with the 3-fold helical structure. Those $\pi$-stacked columns further aggregate into a 2D lattice with hexagonal symmetry. It is likely that due to the space filling requirement, the deficient number of substituents at the imide end drives the molecule to rotate at a certain angle to average the side chain density around the periphery. Therefore, we concluded that that the intrinsic uneven substitution layout of PEI mesogen is responsible for the inevitable 120°
rotation in the DCLC phase.

3.5. Rotation angle and charge carrier mobility

Electronic wave function coupling as the result of frontier orbital overlapping is the key factor that controls the charge transport between $\pi$-conjugated molecules. It was revealed through theoretical calculation that the transfer integral is greatly influenced by the rotational angle when intermolecular $\pi$-stacking spacing is treated as an unchanged variable. It was also calculated that frontier orbitals (HOMO and LUMO) of PEI mesogen are similar to those of the PDI mesogen. This conclusion leads to two consequences. First, the plot of $J^2$ vs. $\varphi$ will remain qualitatively the same. Second, frontier orbitals of PEI compounds remain to be geometrically symmetric. Therefore, orbital overlapping should be similar between the rotation at certain angle and the supplement of it (Figure 3.5.1). PEI compounds are considered as n-type semiconductors, charge transport mainly happens through LUMO-LUMO coupling. As shown in Figure 3.5.1, two $J^2$ maxima are corresponding with cofacial or ca. 67 °, which is fairly close to the 60 ° angle (the supplement of 120 °) found with compound 3b and 3c. Compared to rotation angles characterized for PDI compounds, which is most likely 90 °, the improvement is substantial.
With optimized rotation angle, one should expect that electron hopping becomes more effective and compounds in their DCLC phase should have good charge carrier mobilities. One measurement utilizing ss-TF-SCLC method was carried out with compound 3c and the result is shown in Figure 3.5.2a. The calculation of charge carrier mobility is based on the \( I-V \) characteristic of the semiconducting material. At relatively low voltage, the \( I-V \) relationship is linear (ohmic behavior). As the voltage becomes higher, charge injection will take place and the charge carrier concentration will increase. As the result, the electric field across the semiconducting material could be modulated significantly when the charge carrier concentration is high enough. In this case, the \( I-V \) behavior deviates from ohmic and the current becomes space charge limited. The current density \( J \) and sweeping voltage \( V \) obey the relationship described in the following equation where \( \mu_0 \) is the charge carrier mobility at zero electric field, \( L \) is the active layer’s thickness, \( C \) is the capacitance of the sample per unit area, \( \gamma \) is the electric field coefficient which reflects the change of charge carrier mobility as the electric field changes,
and $\Theta$ is a factor smaller than unity that reflects the reduction of charge carriers due to shallow traps and imperfect ohmic contact between the organic active layer and the electrode.$^5$

\[ I = \frac{q}{\Theta} \Phi \rho \exp \left( \frac{V}{kT} \right) \left( \frac{V}{L} \right) \frac{V^2}{L^2} \]

As we can see from the equation, the $J-V$ relationship is not perfectly quadratic when $\gamma$ is not zero. In fact, the mobility is always electric field dependent and therefore the exponent on $V$ could be higher than 2. The data fitting was done for the region that is close to quadratic and the result is shown in Figure 3.5.2b. While assuming the electron to be the predominant free carrier in the film, the charge carrier mobility at zero electric field was calculated to be $5.24 \times 10^{-4}$ cm$^2$V$^{-1}$s$^{-1}$ and the electric field coefficient $\gamma = 0.0128$ cm$^{0.5}$V$^{-0.5}$.

![Figure 3.5.2.](image)

**Figure. 3.5.2.** (a) $J-V$ curve of the device “ITO/3c/ITO” for the charge carrier mobility calculation (b) Double logarithm plot of $J-V$ curve to show the linear (ohmic behavior) and quadratic (space charge limited) parts

The mobility is only modest mainly because of three reasons. First, both charge injection and depletion electrodes are indium tin oxide (ITO) coated glass. The work function of ITO is
4.5 eV which is around 1.0 eV higher than the LUMO level of compound 3c which is around 3.5 eV. This large difference cannot guarantee an ohmic contact the electrode-sample interface. As the result, it limits the measured mobility.\(^5\) Second, the sample thickness was calibrated by using 10 μm sphere glass spacers between two electrodes. With such a thickness, 3c does not align perfectly into homeotropic domains (Figure 3.5.3). It is well known that the morphology of the sample is crucial to its charge transport properties. Charge carrier mobility could be much higher on a sample that is homeotropically aligned due to the removal of grain boundaries in the path of the charge transport. Third, as will be discussed in a later section, sample 3c experiences crystallization and the π-stack direction will undergo changes. Consequently, the charge transport anisotropy may not favor the vertical conductivity even if the sample was originally aligned homeotropically. It is expected that with proper material employed at charge injecting electrode (eg. silver, with a work function of 4.2 eV) and better sample alignment, the measured charge carrier mobility will be much higher.

**Figure 3.5.3.** PLM picture showing the texture developed from the ITO glass sandwiched sample of 3c, the scale bar in the picture marks 100 μm
3.6. Crystallization and monotropic liquid crystal

As shown in Figure 3.3.9a, a small endothermic peak could be observed upon heating the sample of 3b at a 20 °C/min ramp rate. To explore the nature of the peak, DSC experiments with different heating and cooling rates were carried out. Results are summarized in Figure 3.6.1a. The enthalpy change of the endothermic peak at around 110 °C substantially increases as the ramp rate becomes slower. Furthermore, a broad peak associated with an exothermic transition begins to appear with 5 °C/min ramp rate. These observations could be explained by sample crystallization of compound 3b. At relatively high heating and cooling rate, time needed for ramping down and back up to the clearing point is short enough to avoid crystallization. However, with a slower ramp rate, sample was given longer time to generate nuclei and develop a crystalline phase. Comparing with the metastable LC phase, the crystalline phase is thermodynamically favored below the corresponding melting point. Therefore, the broad exothermic transition is corresponding to the crystallization of the sample at high temperature and the endothermic peak at around 110 °C is corresponding to the melting of the just formed crystalline phase. It is concluded that the shorter OEG units in compound 3b leads to a faster crystallization. No peak associated with crystallization could be observed with compound 3c at a 5 °C/min ramp rate (Figure 3.6.1b). However, samples of both 3b and 3c will eventually crystallize after storing at RT provided with enough time. The difference in the crystallization speeds of two compounds may further lead to a difference in terms of application. Unlike 3c, it is difficult to obtain homeotropic alignment on ordinary glass surface or ITO coated glass with compound 3b. Instead, only dendritic growth can be observed under PLM as shown in Figure 3.3.9c. Thus, applications such as photovoltaic or light emitting diode may be difficult with compound 3b. This drawback may also undermine the electronic performance of compound 3b.
as the elimination of grain boundaries and uniform molecular alignment on a macroscopic scale may be more difficult to achieve. Despite of having the ability of forming homeotropic alignment, 3c suffers from its low clearing point as the operating temperature range is severely limited.

Figure 3.6.1. DSC heating curves at three different ramp rates (20, 10, 5 °C/min) (a) 3b (b) 3c (c) 4a (d) 4b

Improving thermal-stability, LC phase stability and examining the influence of asymmetrical chain length on rotation angle were major incentives to the design of the fourth series of compounds. With the introduction of side chains with different chain lengths (One of
side chains is one OEG repeating unit longer or shorter than the other two), it is expected that the crystallization will be hindered without compromising the clearing point of the compound. PLM, DSC and XRD experiments have been carried out to study the thermodynamic phase behavior and the corresponding phase structure. Thermodynamic parameters are summarized in Table 3.6.1. DSC studies of compounds 4a and 4b with three different ramping rates were used to evaluate the crystallization speed and the result is shown in Figure 3.6.1c and Figure 3.6.1d. First of all, only one endothermic peak associated with small enthalpy and entropy changes could be observed with the slowest ramp rate. Thus, within the detectable range of DSC, both samples of 4a and 4b remained uncry stallized for at least 30 minutes under experiment condition. Crystallization tendency is weakened as side chain packing becomes difficult. It should be noted that although the DCLC phase also prefers uniform space filling, side chains are melted and mobile and the asymmetrical chain length does not affect as largely as it does on the crystalline phase. Secondly, 4a and 4b exhibit increased clearing points which are at 65 °C and 54 °C, respectively, due to the shorter overall chain length compared to 3c. Therefore, we concluded that in this case, introducing side chain with different chain length is an effective way to suppress crystallinity and increase clearing points at the same time.

**Table.3.6.1.** Summary of important thermodynamic parameters of series 4 compounds

<table>
<thead>
<tr>
<th>Compounds</th>
<th>PHASE BEFORE [Phase transition temperature(°C)]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(enthalpy(KJ/mol)/entropy (J/mol<em>K)) PHASE AFTER</em></td>
</tr>
<tr>
<td>4a</td>
<td>Colh<a href="2.4/7.1">65.1</a>Iso</td>
</tr>
<tr>
<td>4b</td>
<td>Colh<a href="2.1/6.4">54.2</a>Iso</td>
</tr>
</tbody>
</table>

*Samples 4a and 4b were measured with ramp rate at 10°C/min
LC phase structures of 4a and 4b were also characterized by 1D and 2D XRD experiments. Results are shown in Figure 3.6.2. Cell parameters are summarized in Table 3.6.2. Despite of lacking unified side chain length, compounds 4a and 4b share same mesophase characteristics with LC 3b and 3c. 2D lattices of supramolecular columns are hexagonal while the three-fold helicity of the intra-column molecular packing also remains the same. This observation supports the argument that the substitution layout of PEI mesogen is the dominant factor that controls the rotation angle of π-stacking in DCLC phases. This is reasonable as the rotation is driven by steric hindrance and space-filling requirement, both of which receive more influence from groups close to the perylene ring than groups far away. In addition, both 4a and 4b are able to form homeotropic alignment on an ITO coated glass substrate as shown in Figure 3.6.3. Generally speaking, compounds with longer substitution tails were found to be easier to stand on an ITO surface.
Figure 3.6.2. (a) RT 1D-integration of XRD pattern of 4a. (c) RT 1D-integration of XRD pattern of 4b. Insets show the indexed weak small-angle diffractions. The peak marked “Si” corresponds to the diffraction from crystalline silicon powder that was added as the calibration standard. (b) Aligned 2-D XRD pattern of 4a at RT. (d) Aligned 2-D XRD pattern of 4b at RT. Samples were melted into isotropic liquid state before experiment to remove thermal history. Shearing direction is pointing up as marked by the arrow.

Table 3.6.2. Cell parameters of DCLC phase of 4a and 4b

<table>
<thead>
<tr>
<th>Compounds</th>
<th>α (β = γ = 90 °)</th>
<th>a=b</th>
<th>c</th>
</tr>
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<tbody>
<tr>
<td>4a</td>
<td>60 °</td>
<td>1.44 nm</td>
<td>0.345 nm</td>
</tr>
<tr>
<td>4b</td>
<td>60 °</td>
<td>1.56 nm</td>
<td>0.345 nm</td>
</tr>
</tbody>
</table>
Figure 3.6.3. (a) PLM picture of 4a (b) PLM picture of 4c Polarized optical microscopic pictures were taken at temperature closely below phase transition upon cooling. Samples were melted into isotropic liquid state followed by cooling down to proper temperature at a rate of approximately 0.05 °C/min. Annealing is required to obtain pure textures. Slow cooling rate is applied in order to improve the alignment. Both pictures were taken with polarizers slightly uncrossed. It is otherwise dark. Scale bars in the picture mark the length of 100 μm.

Compounds 3b, 3c, 4a and 4b form completely crystallized samples after storing at RT for hours or days. Combining with the XRD and DSC results (in which all melting point temperatures of crystalline phases are higher than clearing point temperatures of LC phases), we concluded that all of them behave as monotropic liquid crystals. The DCLC phases formed during cooling from liquid state are meta-stable and will transform to the thermodynamically stable state over time. In order to understand these crystallization processes, we used 2D XRD to analyze structures of crystallized samples of 3b and 3c. To acquire more information, samples were first sheared in their DCLC phases followed by storing at RT over 3 days before 2D XRD experiments were performed on the pre-aligned crystalline fibers. Results were summarized in Figure 3.6.4. Measurements with incident X-ray beam along three directions generated three
different patterns named as through-view (TD), shear-view (SD) and edge-view (ED), respectively. Previously shown LC fiber patterns were all collected with X-ray beam coming from TD and therefore could be directly compared with the crystallized TD pattern. In contrast with results from aligned LC samples, RT annealed samples of 3b and 3c exhibit multiple sharp diffractions at quadrants indicating the 3D crystalline order. However, there is a crucial difference between two crystallized samples regarding the molecular orientation. In the pattern of crystallized 3b, diffraction arising from \( \pi \)-stacking order remains to appear exclusively on meridional axis. This indicates that the direction of column axes did not undergo any changes as the sample crystallized. Further evidence could be obtained with SD pattern of 3b, in which none of diffractions was found to be originated from the \( \pi \)-stacking order. This is because electron density variation along the incident X-ray beam direction is impossible to satisfy Bragg’s law at any circumstances. Thus, the XRD result suggested that the \( \pi \)-stacking direction remained to be parallel to the substrate as the sample fully crystallized. In contrast, an obvious rearrangement of \( \pi \)-stacking direction was discovered with compound 3c as evidenced by the existence of dispersed relatively weak but sharp diffraction arcs over 360° at 2\( \theta \) angles that were originally associated with \( \pi \)-stacks. Also supported by SD and ED patterns, we speculated that the columnar structure may be lost during the crystallization process and the \( \pi \)-stack could no longer maintain a uniformed direction.
Although the crystallizing behavior of compounds 3b and 3c deviate from our designing purpose and reasons behind different rearrangements during crystallization remain unclear to us, these results may lead to a valuable implication. Single crystalline material suffers from high

Figure 3.6.4. (a) 2D XRD diffraction of crystallized fiber of 3b (left to right: TD, SD, ED). (b) 2D XRD diffraction of crystallized fiber of 3c (left to right: TD, SD, ED) Schematic drawing at the bottom illustrates the relationship of shearing direction to X-ray incident beam direction.
fabrication cost and lacking of physical flexibility, while polycrystalline material’s electronic properties are limited by domain boundaries and lack of uniform molecular orientation. On the contrary, LC material is known for its stimuli-responsiveness, facile processability, less domain boundary and self-healing properties. Charge carrier mobilities of such materials could approach the value of single crystalline organic semiconductors. However, the side chain motion disturbs the order of $\pi$-stack in the DCLC phase which often leads to substantial decrease in charge carrier mobility compared to the crystalline phase. The structural disorder of the columnar packed molecules should be considered as the major drawback of DCLC materials used for charge transport. It should be noted that it is the same molecular mobility that gives rise to the abovementioned advantages that are attractive and unique to this class of materials. Strategies were developed by using gelators or spacers to constrain the core fluctuation or to decouple the core from the side chain motion. However, they only alleviate but not eliminate the problem. With monotropic liquid crystal, however, this dilemma may be tricked by the tool of time. Thin film electronic devices can be made by aligning $3b$ in its LC phase and allowing the sample to crystallize over a short time at RT. The $\pi$-stacking order is improved to have less fluctuation as the result of the formation of 3D crystalline lattice while molecular alignment does not have to be sacrificed. Moreover, the orientation of $\pi$-stack gets retained. Such property and consequent manufacturing technique are easily accessible with monotropic LC materials as they offer simple approaches to combine device-scale molecular alignment and highly ordered $\pi$-stack. Depending on the method applied to align the sample of $3b$ (through shearing or through melting), thin film crystalline $3b$ may have great potential to be a candidate of the active component in FET devices (which prefer the conducting channel to be parallel to the dielectric substrate) or photovoltaic and light emitting diode devices (which usually require homeotropic
alignment).

3.7. Self-aggregation as water soluble supramolecular polymer

Oligomeric ethylene glycol is known for its good solubility in various organic solvents as well as in water. As the result of OEG substitution, compounds 3b, 3c, 4a and 4b have good solubility in almost all organic solvent systems except nonpolar alkanes. Water solution having concentration as high as 1 g/L could be obtained with all four compounds. Revealed by fluorescence spectra, extensive aggregations of those compounds were found in water solution even at very low concentration. Using water solution of 3b as the example, the gradual change in spectrum was recorded in Figure 3.7.1 as concentration increases from $3.632 \times 10^{-6}$ mol/L to $1.134 \times 10^{-4}$ mol/L. The first noticeable change is the gradual disappearance of peak with $\lambda_{\text{max}}$ at 544 nm. This could be explained by the decrease of free monomer concentration in water solution due to supramolecular aggregation. At the same time, a new peak at 649 nm becomes the major emission band which is likely to be associated with oligomeric species in the solution. Therefore compounds 3b, 3c, 4a and 4b form supramolecular polymeric material in their water solutions. Such systems may combine properties from conventional polymeric material such as mechanical strength with those arise from the supramolecular self-assembly, such as reversibility and responsiveness to external stimulus.\(^{50}\)
To study and characterize the water soluble supramolecular polymer, we used an aggregation model involving two steps of polymerization. First, two monomeric molecules form dimer with a dimerization constant $K_2$. Consequently, the dimer polymerizes into longer oligomer by connecting with one monomer at a step with an association constant $K$ which is assumed to be independent of the polymer chain length. The model of dimerization and chain-growth polymerization is described with equations 1 and 2. $[M_1]$ and $[M_2]$ is the concentration of free monomer and dimer, respectively. $[M_n]$ and $[M_{n+1}]$ represent concentrations of polymers with $n$ or $(n+1)$ repeating units. The total concentration of solution $(C_0)$ is the sum of concentration of molecules from each species (equation 3). Therefore, the relationship of monomer concentration, dimerization constant and association constant could be expressed by equation 4. To calculate $K_2$ and $K$, it is necessary to measure $[M_1]$ in a series of solutions with
known total concentration $C_0$.

\[
K_2 = \frac{[M_2]}{[M_1][M_1]} \tag{①}
\]

\[
K = \frac{[M_{n+1}]}{[M_1][M_n]} \tag{②}
\]

\[
[M_2] + 2[M_3] + 3[M_3] + \cdots + \mu[M_n] + \cdots = c_d \tag{③}
\]

\[
C_0 = [M_1](1 + \frac{K^2}{K} \left(1 - \frac{1}{K[M_1]^2}\right)^2 - 1) \tag{④}
\]

Integration of fluorescence intensity has a linear relationship to the concentration of chromophore in solution. It is assumed in our calculation that the fluorescence intensity at 518 nm ($I_{518}$) reflects the concentration of free monomer in solution as shown in equation 5. However, this relationship does not hold when chromophoric molecules aggregate. Due to extensive aggregation, 3c form oligomers even at concentration as low as $10^{-9}$ mol/L. Therefore, $\alpha$ cannot be directly obtained by measuring diluted water solution of 3c. On the other hand, molecules of 3c remain in their monomeric form at much higher concentrations ($\sim 3 \times 10^{-6}$ mol/L) when using ethanol as the solvent due to weakened $\pi-\pi$ interaction. In this case, $C_0 = [M_1]$, the range of $\alpha$ could be estimated. Corrections and adjustments need to be done with fluorescence intensity in ethanol solution as it does not equal the intensity measured in water solution. Although the fluorescence spectrum of 3c in ethanol is quite similar to that in water, there is a shift in wavelength. Moreover, the quantum efficiencies are different in two solutions due to the difference in their dielectric constants. Therefore, $I_{518}$ could be approached by two corrections as shown in equation 6.

\[
[M_1] = \alpha \times I_{918} \tag{⑤}
\]
Quantum efficiency (QE) measurements were carried out using standard compound rhodamine b with a known QE of 31% in water solution. Rhodamine b was selected for good overlap of the absorption and emission spectra between sample and reference (Figure 3.7.2.). Four ethanol-water solutions of $3c$ were prepared to have increase of volume percentage of water from 0% to 50% to gradually approach the QE in the pure water solution. Results were summarized in Table 3.7.1. In QE calculations, all solutions are diluted enough to ensure the absorption at excitation wavelength to be lower than 0.1 to avoid inner filter effect.

![UV and Fluorescence spectra of rhodamine b and 3c in solutions. Spectra have been normalized to have equal intensity at $\lambda_{\text{max}}$.](image)

**Figure 3.7.2.** UV and Fluorescence spectra of rhodamine b and $3c$ in solutions. Spectra have been normalized to have equal intensity at $\lambda_{\text{max}}$.  

**Table 3.7.1.** Quantum efficiency of $3c$ in ethanol and in ethanol-water mixture (rhodamine b water solution is measured as the QE standard)

<table>
<thead>
<tr>
<th>Solution</th>
<th>Quantum Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rhodamine b in H$_2$O</td>
<td>31%</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>------------</td>
<td>----------------</td>
</tr>
<tr>
<td><strong>3c</strong> in ethanol</td>
<td></td>
</tr>
<tr>
<td>3c in ethanol-H$_2$O (90% vol. Et)*</td>
<td></td>
</tr>
<tr>
<td>3c in ethanol-H$_2$O (80% vol. Et)*</td>
<td></td>
</tr>
<tr>
<td>3c in ethanol-H$_2$O (50% vol. Et)*</td>
<td></td>
</tr>
</tbody>
</table>

* Volume percentage of ethanol in ethanol-water mixture

QE increases as dielectric constant of solvent increases. Dielectric constants of ethanol and water are about 24 and 80 around RT. It is expected to see the increase of QE as the mixture approaches pure water solution. However, QE starts to decrease when the volume of ethanol is lowered to 80%. Furthermore, although apparent change of the spectrum’s shape was not observed, there are slight red shifts of $\lambda_{\text{max}}$ in both UV and fluorescence as the volume percentage of water became greater. Considering the possible aggregation, the real quantum efficiency of monomeric 3c in pure water solution should have the lower limit of 89% while the maximum should be limited at 100% (theoretical). Correction factor was measured to be 0.503 as shown in Figure 3.7.3. Emission spectra were normalized to have same intensities at $\lambda_{\text{max}}$. 
Figure 3.7.3. Fluorescence spectra of rhodamine b and 3c in solutions. Spectra have been normalized to have equal intensity at $\lambda_{\text{max}}$.

Eleven samples of water solution of 3c were prepared with concentrations covering the range from about $1 \times 10^{-6}$ mol/L to $3 \times 10^{-9}$ mol/L. Fluorescence spectra were obtained and shown in Figure 3.7.4. By comparing the emission intensity at 518 nm with the determined $I_{518}$, $[M_1]$ could be obtained for each solution sample. Plots of $[M_1]$ vs. $C_0$ for 3b and 3c are shown in Figure 3.7.5. Calculated $K_2$ and $K$ are summarized in Table 3.7.2. While association constant $K$ are similar, the higher value of dimerization constant may be due to relatively poor solubility (lower hydrophilicity) of compound 3b in water solution.
Figure. 3.7.4. Fluorescence spectra of 3c in water solutions
Figure 3.7.5. (a) Plot of $C_0$ against $[M_1]$ for compound 3b (b) Plot of $C_0$ against $[M_1]$ for
compound 3c.

Table 3.7.2. Lower limit of $K_2$ and $K$ calculated from curve fitting

<table>
<thead>
<tr>
<th>Compounds</th>
<th>$K_2$ (mol$^{-1}$•L$^{-1}$)</th>
<th>$K$ (mol$^{-1}$•L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3b</td>
<td>2.92×10$^7$</td>
<td>4.36×10$^6$</td>
</tr>
<tr>
<td>3c</td>
<td>7.95×10$^6$</td>
<td>5.06×10$^6$</td>
</tr>
</tbody>
</table>

3.8. Conclusion

OEG substituted PEIs were designed and synthesized. Monotropic liquid crystallinity was found with compound 3b, 3c, 4a and 4b, respectively. LC materials were easy to align and generally capable of forming homeotropic alignment on ITO coated glass. With asymmetrical substitution mode, the clearing point was increased while keeping a relatively low crystallization tendency. For all four LC compounds, a 120° (or the supplement 60°) rotation angle was revealed by 2D XRD and force field simulation. Compared with rotation angles of 90°, which was found with LC PDIs, the electronic wave function coupling is substantially improved according to theoretical calculations when holding other conditions the same (e.g. π-stacking spacing). It was also discovered that the overall molecular alignment could be maintained while samples of 3b experience crystallization. Combining high π-stacking order, macroscopic molecular orientation and good processability, it makes monotropic DCLC 3b the promising candidate as organic charge transport material or acceptor in photovoltaic cells. Finally, the supramolecular assemblies of 3b and 3c were studied in their water solutions. Large association constants were calculated suggesting extended aggregations in solution.
3.9. Experimental section

Instrumental analysis and characterization

$^1$H NMR spectra were recorded on a Varian 600MHz NMR spectrometer, with deuterated chloroform (CDCl$_3$) as solvent at 25 °C. The chemical shifts were reported using chloroform as the internal standard. The NMR graphs and data were collected by using Spinworks 3 software. The peak at 7.26 ppm with two satellite peaks belongs to CHCl$_3$ residue and the peak at 1.58 ppm belongs to H$_2$O.

High resolution mass spectra (HRMS) were obtained at CUNY Mass Spectrometry Facility at Hunter College.

Fourier transfer infrared spectra (FTIR) were recorded on a Bruker Vertex 70V spectrometer at the resolution of 1 cm$^{-1}$. A Thermo Electron 0019-200 heating cell (controlled by a Glas-Col DigiTrol II temperature controller) was used to heat specimen to collect FTIR spectra at high temperatures (HT).

Fluorescence spectra were obtained at RT on a JOBIN YVON Co. FluoroMax-3 spectrofluorometer with slits setting at 5 nm for both excitation and emission. Solution samples were all freshly prepared for measurements. Neat samples were heated to isotropic state on a quartz plate followed by cooling to RT in order to remove the thermal history.

All XRD measurements were performed at RT on a Bruker Nanostar instrument with a Cu K$_\alpha$ source. A VÂNTEC 2000 2D detector and an image plate were used as small and wide angle detectors, respectively. Powder LC samples for XRD studies were prepared by first
heating up to isotropic liquid state, then cooling down to RT. Aligned LC samples were obtained by mechanical shearing of powder LC samples. The crystallized samples were prepared by allowing aligned LC samples to crystallize over hours to days. The typical X-ray exposure time is 8 hours for an oriented crystalline sample.

Polarized light microscopy picture shown in Figure 1 was taken from a Leica DM LB2 microscope equipped with a Leica DGC 320 camera and a Mettler Toledo FP82HT hotstage (controlled by a Mettler Toledo FP90 central processor). Samples were heated beyond their clearing points and cooled down slowly at approximately 0.03°C/min ramp rate to temperature closely below phase transition.

DSC experiments were performed on a Perkin-Elmer PYRIS Diamond differential scanning calorimeter. Transition temperatures were determined using onset temperatures and were calibrated using standard material (indium).

UV-visible spectra were collected on a PerkinElmer Lambda UV-Vis spectrometer at the resolution of 1 nm.

**Materials and Synthesis**

All reagents were used as received. 1-bromooctane (98%), 1-bromodecane (99%), 1-bromo-3,7-dimethyloctane (98%), 1-bromododecane (98%) were purchased from Acros Organics. 2-methoxylethanol (98%), 2-(2-methoxyethoxyl)ethanol (98%), 2-(2-(2-methoxyethoxyl)ethoxyl)ethanol (98%), dimethyl sulfoxide (98%), 1,8-Diazabicyclo[5.4.0]undec-7-ene (99%), 4-Toluenesulfonyl chloride (99%) were purchased from Sigma Aldrich.

General synthesis procedure for 1a, 1b, 1c and 2a is outlined below:
General synthesis procedure for 3a, 3b and 3c is outlined below:

An alternate way of synthesizing 3a, 3b and 3c was later found out and is outlined below:

General synthesis procedure for 4a and 4c is outlined below:
General procedure of 1a, 1b, 1c and 2a

Into a 25 ml Schlenk flask were added 196 mg (0.5 mmol) perylenetetracarboxylatemonoimidemonoanhydride (PTMIMA) (391.33 g/mol), 138 mg (1 mmol) of potassium carbonate (138.205 g/mol) and 10ml of distilled water. The mixture was purged with N₂ when it was heated to reflux overnight. Subsequently, to the solution was added corresponding alkyl bromide (4 mmol) and 17 mg (0.1 mmol) potassium iodide (166.0028 g/mol). The mixture was then stirred vigorously and heated to reflux for 3 hours under nitrogen protection. The reaction was stopped by cooling down to RT and two layers will separate. Take away the lower colorless water layer by Pasteur pipette. 15 ml of methanol was then added to the flask for precipitation. Subsequently, the solid was collected on a Buchner funnel by suction filtration and rinsed by 5ml of methanol. The solid was dissolved in chloroform and purified by column chromatography (Rf = 0.2, 1/200, methanol/chloroform). The final orange to red solid was dried in vacuum oven at 50 °C until constant weight.

General procedure 1 of 3a, 3b and 3c

Into a 10ml Schelenk flask were added 196 mg (0.5 mmol) PTMIMA (391.33 g/mol), 12.5 mmol corresponding polyethyleneglycolmonomethylether (OEGMME), 3.75 mmol corresponding polyethyleneglycolmonomethylthertosylate (OEGMMET) and 193 mg (1.4
mmol) of potassium carbonate (138.205 g/mol). The mixture was heated to 70 °C for 48 hours under nitrogen protection. The unreacted PTMIMA was then removed by dissolving the reaction mixture into chloroform and filtered with vacuum. The filtrate was concentrated on the rotary evaporator and purified through a thick short column to remove most of tosylate and high polar impurities. The crude product was then dissolved in 15ml of distilled water and precipitated by adding NaCl to the solution. The sticky solid was collected on the Buchner funnel by suction filtration. The precipitation process was repeated for an additional 2 times. The solid was then purified through column chromatography (R_f = 0.1, 1/33, methanol/chloroform). The final red sticky solid was dried in vacuum oven at 50°C until constant weight. With this method, percent yields (isolated yield) of 26% and 43% were obtained for compounds 3b and 3c, respectively.

**General procedure 2 of 3a, 3b and 3c**

Into a 10ml Schlenk flask were added 196 mg (0.5 mmol) perylenetetracarboxylatemonoimidemonoanhydride (PTMIMA) (391.33 g/mol), 696 mg (1.475 mmol) tetrabutylammonium hydroxide (55% w.t. water solution) (259.47 g/mol) and 5ml DMSO. To allow a complete dissolving of the PTMIMA, the mixture was heated to 40 °C for 3 hours under nitrogen protection. Subsequently, 2 mmol of the corresponding OEGMMET was added into the purple pink solution. The solution was then heated to 60 °C for 48 hours under nitrogen protection. After cooling down to RT, the reaction mixture was transferred to a 125 ml separatory funnel and the reaction vessel was rinsed by a small amount of chloroform which was later combined with the mixture into the funnel. Along the inner wall of the funnel was added slowly with a pipette 50 ml of distilled water and then swirled gently to allow the DMSO to diffuse into the water layer. Repeat the washing process for an additional 2 times. The leftover organic layer was purified through column chromatography (R_f = 0.1, 1/33, methanol/chloroform). The final
red sticky solid was dried in vacuum oven at 50 °C until constant weight.

General procedure 2 of 4a and 4c

Corresponding OEGMMETs, DBU and DMSO were dried in advance with 4A beads molecular sieve in the desiccator for more than 48 hours. Corresponding alcohols are freshly distilled with freshly cut metal sodium stripes and used immediately. The entire reaction process was under argon protection. To the mixture of 145 mg (0.95 mmol) DBU (152.24 g/mol), 196 mg (0.5 mmol) PTMIMA and 5 ml DMSO in a 25 ml Schelenk flask were added 40 mmol freshly distilled corresponding alcohol (OEGMME). The mixture was heated at 60 °C for 3 hours after which was added with 2 mmol corresponding OEGMMET. The reaction temperature was then increased to 80 °C for 48 hours. After cooling down to RT, the reaction mixture was transferred to a 125 ml separatory funnel and the reaction vessel was rinsed by a small amount of chloroform which was later combined with the mixture into the funnel. Along the inner wall of the funnel was added slowly with a pipette 50 ml of distilled water and then swirled gently to allow the DMSO and the excess amount of alcohol to diffuse into the water layer. Repeat the washing process for an additional 2 times. The leftover organic layer was purified through column chromatography (R_f = 0.1, 1/33, methanol/chloroform). The final red sticky solid was dried in vacuum oven at 50 °C until constant weight.

1H NMR:

3c:

1H NMR (CDCl3, 600 MHz): δ (ppm) = 8.64 (d, J = 8.44 Hz, 2H, Ar), 8.50 (m, 4H, Ar), 8.17 (d, J = 7.21 Hz, 2H, Ar), 4.50 (t, J = 4.82 Hz, 4H, -COO-CH2-CH2), 4.47 (t, J = 6.06 Hz, 2H, -N-CH2CH2), 3.88 – 3.46 (m, 30H, -OCH2CH2), 3.36 (s, 6H, CH3), 3.31 (s, 3H, CH3).
3b:
\[ ^1H \text{ NMR (CDCl}_3, 600 \text{ MHz): } \delta \text{ (ppm) = 8.60 (d, J = 8.10 Hz, 2H, Ar), 8.43 (m, 4H, Ar), 8.14 (d, J = 8.00 Hz, 2H, Ar), 4.51 (t, J = 4.96 Hz, 4H, -COO-CH}_2\text{-CH}_2, 4.48 (t, J = 6.47 Hz, 2H, -N-CH}_2\text{CH}_2), 3.89 \text{ – 3.54 (m, 18H, -OCH}_2\text{CH}_2), 3.38 (s, 6H, CH}_3, 3.33 (s, 3H, CH}_3). \]

3a:
\[ ^1H \text{ NMR (CDCl}_3, 600 \text{ MHz): } \delta \text{ (ppm) = 8.66 (d, J = 7.83 Hz, 2H, Ar), 8.50 (m, 4H, Ar), 8.17 (d, J = 7.89 Hz, 2H, Ar), 4.49 (m, 6H, -COO-CH}_2\text{-CH}_2, -N-CH}_2\text{CH}_2), 3.77 (m, 6H, -OCH}_2\text{CH}_2), 3.44 (s, 6H, CH}_3, 3.41 (s, 3H, CH}_3). \]

1a:
\[ ^1H \text{ NMR (CDCl}_3, 600 \text{ MHz): } \delta \text{ (ppm) = 8.61 (d, J = 8.14 Hz, 2H, Ar), 8.45 (m, 4H, Ar), 8.11 (d, J = 7.94 Hz, 2H, Ar), 4.33 (t, J = 7.03 Hz, 4H, -COO-CH}_2\text{-CH}_2), 4.19 (t, J = 7.52 Hz, 2H, -N-CH}_2\text{CH}_2), 1.83 \text{ – 1.27 (m, 36H, CH}_2), 0.88 (m, 12H, CH}_3). \]

1b:
\[ ^1H \text{ NMR (CDCl}_3, 600 \text{ MHz): } \delta \text{ (ppm) = 8.62 (d, J = 8.01 Hz, 2H, Ar), 8.47 (m, 4H, Ar), 8.11 (d, J = 8.00 Hz, 2H, Ar), 4.33 (t, J = 6.884 Hz, 4H, -COO-CH}_2\text{-CH}_2), 4.20 (t, J = 7.68 Hz, 2H, -N-CH}_2\text{CH}_2), 1.81 \text{ – 1.26 (m, 48H, CH}_2), 0.87 (m, 12H, CH}_3). \]

1c:
\[ ^1H \text{ NMR (CDCl}_3, 600 \text{ MHz): } \delta \text{ (ppm) = 8.56 (d, J = 8.15 Hz, 2H, Ar), 8.39 (m, 4H, Ar), 8.08 (d, J = 7.96 Hz, 2H, Ar), 4.34 (t, J = 6.80 Hz, 4H, -COO-CH}_2\text{-CH}_2), 4.19 (t, J = 7.68 Hz, 2H, -N-CH}_2\text{CH}_2), 1.83 \text{ – 1.25 (m, 60H, CH}_2), 0.87 (t, J = 6.91 Hz, 12H, CH}_3). \]

2a:
\[ ^1H \text{ NMR (CDCl}_3, 600 \text{ MHz): } \delta \text{ (ppm) = 8.62 (d, J = 7.96 Hz, 2H, Ar), 8.47 (m, 4H, Ar), 8.10 (d, J = 7.98 Hz, 2H, Ar), 4.38 (m, 4H, -COO-CH}_2\text{-CH}_2), 4.22 (m, 2H, -N-CH}_2\text{CH}_2), 1.87 \text{ – 0.86 (m,} \]
18H, CH\textsubscript{1}, CH\textsubscript{2}), 1.04 (d, 3H, -N-CH\textsubscript{2}-CH\textsubscript{2}-CH(CH\textsubscript{2})-CH\textsubscript{3}), 0.98 (d, 6H, -COO-CH\textsubscript{2}-CH\textsubscript{2}-CH(CH\textsubscript{2})-CH\textsubscript{3}), 0.86 (d, 18H, -CH-CH\textsubscript{3}).

4a:

\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 600 MHz): \(\delta (ppm) = 8.66 (d, J = 8.05 \text{ Hz}, 2H, \text{Ar}), 8.50 (t, J = 7.45 \text{ Hz}, 4H, \text{Ar}), 8.20 (m, 2H, \text{Ar}), 4.55 (m, 6H, -COO-CH\textsubscript{2}-CH\textsubscript{2}, -N-CH\textsubscript{2}CH\textsubscript{2}), 3.96 – 3.59 (m, 14H, -OCH\textsubscript{2}CH\textsubscript{2}), 3.49 (s, 3H, CH\textsubscript{3}), 3.44 (s, 3H, CH\textsubscript{3}), 3.39 (s, 3H, CH\textsubscript{3}).

4b:

\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 600 MHz): \(\delta (ppm) = 8.66 (d, J = 8.05 \text{ Hz}, 2H, \text{Ar}), 8.50 (t, J = 7.83 \text{ Hz}, 4H, \text{Ar}), 8.19 (d, J = 7.94 \text{ Hz}, 2H, \text{Ar}), 4.54 (m, 6H, -COO-CH\textsubscript{2}-CH\textsubscript{2}, -N-CH\textsubscript{2}CH\textsubscript{2}), 3.95 – 3.56 (m, 22H, -OCH\textsubscript{2}CH\textsubscript{2}), 3.43 (s, 3H, CH\textsubscript{3}), 3.40 (s, 3H, CH\textsubscript{3}), 3.38 (s, 3H, CH\textsubscript{3}).

3.10. References


2006, 18 (16), 3715-3725.


CHAPTER 4. ENANTIOTROPIC LC PERYLENE DIESTER MONOIMIDES (PEI) WITH BRANCHED ALIPHATIC SUBSTITUTION-TUNNING THE ROTATION ANGLE

4.1. Introduction

Compared to the crystalline material, compounds exhibiting LC phase have properties such as low cost facile fabrication and processability, self-healing and response to external stimulus. It is desired that the temperature range of the LC phase could be well controlled by tuning the molecular structure so that conditions required by applications could be satisfied. For instance, the material should have reasonable clearing point to avoid unwanted isotropization (e.g., remain in the LC phase at relatively high operational temperature). Other morphology changes during device operation are also not desired as they may lead to substantial change of properties and result in the compromise or even failure of the function. On the other hand, the compound should melt easily into isotropic liquid phase to allow low cost device fabrication and processing, as well as to avoid complication associated with high temperature such as chemical decomposition and so on.

As candidates of organic charge transport semiconducting material in electronic or optoelectronic devices, OEG substituted PEIs were studied in the previous chapter. A $120^\circ (60^\circ)$ rotation angle was identified in the LC phases of compound $3b$, $3c$, $4a$ and $4b$. It is believed that this rotation is induced by the substitution layout of PEI mesogens. The non-orthogonal relationship of adjacent aromatic cores implicates an improved electronic coupling and thus more efficient intra-column charge carrier hopping. However, all LC compounds exhibit monotropic
behavior. Although the crystalline tendency could be suppressed by employing chemically asymmetrical substitution, enantiotropic LCLC phase could not be obtained. Moreover, because of a relatively high surface energy associated with the OEG tail, a delicate control of cooling and annealing conditions is required to form homeotropic alignment on ITO coated glass substrates.

In this chapter, we will discuss our design, synthesis and characterization of PEI derivatives with branched aliphatic substitution. Upon the introduction of the branching site on side chains, enantiotropic liquid crystals with high LC phase stability could be obtained. Such materials are advantageous as they are water-safe, chemically stable, having wider LC phase temperature range and much easier homeotropic alignment.

Furthermore, as will be discussed later, the incorporation of branched side chains with relatively short chain length will lead to a 72° rotation angle, which is considered to be another improvement in electronic coupling as the transfer integral $J^2$ has a larger value at this angle.

4.2. Molecular design

The challenge faced by the molecular design is evidenced by the linear aliphatic or PEG substituted PEIs. Self-assembly of PEIs is complicated by limited number of substitutional sites and the low symmetry topological shape of the molecule. The formation of DCLC phase is driven by strong $\pi$-$\pi$ interaction. But at the same time, the space filling requirement must be satisfied by proper side chain substitution. Linear alkyl chains are too rigid to effectively wrap the surface of columnar aggregate and thus not able to support the DCLC phase. On the other hand, due to small number of substitutions and limited chain length (longer methyl-capped OEG chains are much less available and the incorporated PEI compound may have a clearing point lower than RT), PEG tails also failed to give rise to enantiotropic LC materials.
Incorporation of the branched tails with branching carbon near the rigid aromatic core has been known to cause steric hindrance and to disturb the intra-column molecular packing.\textsuperscript{1,2} The control of the branching position and the chain length could lead to dramatic changes of the thermotropic behaviour of the LC phase. Furthermore, branched substituents have much larger cross sectional area which is much more space filling and could increase the interface curvature needed for a DCLC PEI, considering its inherent substitution-site-deficiency. Therefore, we designed four compounds with structures illustrated in Figure 4.2.1. Compounds \textbf{S1, S2} and \textbf{S3} feature symmetric swallow tails with increasing chain length. Swallow tail used in \textbf{S4} has the same total number of carbons compared to that in \textbf{S2}, but has one side chain with two carbons longer than the other two chains.

\begin{figure}[h]
  \centering
  \includegraphics[width=\textwidth]{structure.png}
  \caption{Molecular structures of branched alkyl substituted PEI compounds}
\end{figure}

\section*{4.3. Thermal properties and phase behaviors}

PLM, DSC and XRD experiments have been carried out to study the thermodynamic phase behavior and the corresponding phase structure. PLM pictures are summarized in Figure 4.3.1. Samples were heated to isotropic liquid state to remove thermal history. The phases that
were obtained and observed in PLM experiments were developed from isotropic liquid states. Self-assembly may happen during cooling process as molecules have relatively high mobility in their liquid state or high temperature condensed state. Hexagonal dendritic textures developed by Compounds S2 and S3 suggested the formation of DCLC phase as samples cooled down from liquid state. However, compound S1 and S4 were optically isotropic after cooling down to room temperature. It’s worth mentioning that the homeotropic alignment with S2 and S3 (especially S3) was extremely easy to obtain. For a thin layer of sample (ca. 1 μm), no annealing or slow cooling is required.

**Figure 4.3.1.** PLM pictures of S1 (a), S2 (b), S3 (c), and S4 (d). Pictures b and c were taken at temperature closely below phase transition upon cooling. Pictures a and d were taken at room
Samples of S1, S2 and S3 were melted into isotropic liquid state followed by cooling down to proper temperature at a rate of approximately 1 °C/min. Sample S4 was cooled on a cold metal surface to achieve fast cooling. Pictures b and c were taken with polarizers slightly uncrossed. They are otherwise dark. Scale bars in the picture mark the length of 100 μm.

To further understand the thermal behaviors of four compounds, DSC experiments were performed and the results are shown in Figure 4.3.2. With small entropy and enthalpy changes and small undercooling, compounds S2 and S3 exhibit heating and cooling curves typical for DCLC materials. In contrast, S4 exhibit no observable peak on both heating and cooling traces. Combining with the dark PLM picture, we speculated that compound S4 fails to form crystalline or LC phase. Instead, it stayed amorphous and therefore was optically isotropic. Compound S1 behaves similarly but more complicated than S4. The material crystallizes not upon cooling, but during heating. The exothermic peak at about 87 °C is associated with this crystallization. The just formed crystallized phase is melted at 160 °C as detected by an endothermic peak with similar enthalpy change. No LC phase was discovered with S1 whatsoever.
Figure 4.3.2. DSC traces of compound S1 (a), S2 (b), S3 (c), S4 (d) with ramp rate at 10°C/min.

Samples were heated to isotropic state before measurements to eliminate thermal history.

Compounds S2 and S3 are enantiotropic DCLC materials as evidenced by the first heating curve of the DSC experiments (Figure 4.3.3). Samples of all four compounds were obtained by evaporating solvent from the corresponding chloroform solution. It is usually considered that molecules dissolved in solution have higher mobility than in neat liquid state. Although the structure of solution cast phase is affected by numerous factors from environment, it sometimes better resembles the thermodynamically stable structure that takes long time to develop in thermally processed condensed state. As shown in Figure 4.3.3b for compound S2, an endothermic peak with large enthalpy and entropy changes could be observed at relatively low temperature below the phase transition to the isotropic liquid. This should correspond to the melting of the crystalline phase into a LC phase. Since the phase transition temperature is lower than that of final isotropization, the DCLC phase is enantiotropic. The fact that no crystallization peak was observed during cooling could be due to very slow crystallization speed. For this reason, at 10°C/min ramp rate, only transitions observable in a DSC experiment after the first.
heating are the forming and melting of the DCLC phase. On the other hand, the qualitatively same first and second heating from the DSC results of S3 suggested very similar phase structures developed through solvent evaporation or through cooling (Figure 4.3.3c). It is concluded that under both conditions, S3 does not enter crystalline phase even at low temperature (0 °C). As we did not observe any crystallization related phase transitions in the temperature range of -50 to 220 °C, it is safe for us to assume the enantiotropic nature of the DCLC phase of compound S3.

The first heating of compounds S1 and S4 behave differently from their second heating. At least three endothermic peaks and one exothermic peak could be identified for compound S1 as shown in Figure 4.3.3a. The phase transition at 161.4 °C is reproducible in the second heating with similar enthalpy change and onset, implying a similar phase structure (probably a crystalline phase based on the relatively large enthalpy change) at high temperature before the final transition. However, the “adjustments” before entering this phase are quite different between samples obtained through evaporation and cooling. It is likely that S1 is only able to develop some ordered structures at a very slow rate during cooling and crystallize in the heating process afterwards at around 101 °C. As to compound S4, two overlapping transitions at temperature below isotropization were identified as shown in Figure 4.3.3d. Although no peak could be observed above them, the sample remains to be solid and optically anisotropic until around 135~140 °C during which the compound gradually transforms into a flowable isotropic liquid. Thus, the sample of S4 may experience a transition from the crystalline state to a phase that is highly disordered. The endothermic peak with 15.2 kJ/mol enthalpy change is not reproducible once the compound is being melted (unless dissolved again), which might be due to extremely slow crystallization speed.
4.4. Structural analysis and discussion

Starting from enantiotropic LC materials S2 and S3, we will discuss the nature of the condensed phase of each compound and the relationship with their structures. 1D and 2D XRD patterns of sheared samples of S2 and S3 are shown in Figure 4.4.1. Hexagonal DCLC phases for both compounds could be assumed from results of 1D integration. Setting the first diffraction peak which has the smallest q value as (10), weak small angle diffractions were indexed as (11),
(20) and (21) for compound \textbf{S2} and (11) and (21) for compound \textbf{S4}. Cell parameters were also calculated and summarized in Table 4.4.1. Three small but sharp diffractions in the range of 1.25 to 1.7 Å\(^{-1}\) (q value) over the broad scattering are from impurities on the aluminum foil which was used as the substrate in the XRD experiments. Two major sharp diffractions at wide angle are corresponding to the \(\pi\)-stacking of PEI molecules and Si powder as the internal standard. The broad and smooth scattering in the range of 1.25~1.7 Å\(^{-1}\) suggested isotropically melted side chains. Therefore, hexagonal DCLC phases were confirmed for compounds \textbf{S2} and \textbf{S3}.

As shown in 2D XRD patterns in Figure 4.4.1b and d, diffractions from (10), (11), (20), (21) planes of 2D hexagonal lattice are all positioned on the equatorial axis. In contrary, strong \(\pi\)-stacking diffraction at wide angle peaks on the meridional axis. These findings agree with common observations that supramolecular columns in DCLC phase are usually aligned parallel with the substrate and the force direction when mechanical shearing force is applied. Non-split \(\pi\)-stacking diffraction indicates that the plane of discotic mesogen is perpendicular to the column’s axis. Diffused scatterings in the range of 1.25~1.7 Å\(^{-1}\) form a halo with uniform intensity distribution over 360 °, suggesting a non-orientated side chain packing despite a highly oriented column packing, which should be attributed to their liquid-like properties. The diffused diffractions on the quadrants originate from intra-column inter-molecular relationships. However, 3D crystalline order does not exist as all of them are very diffuse, which means that the corresponding structures are of short-range. A difference between \textbf{S2} and \textbf{S3} was noticed on these quadrants diffractions from which intra-column supra-structure could be inferred. For compound \textbf{S3}, the projections of four quadrant diffractions on the meridional axis have the d-spacing of 1.03 nm which is exactly three times as the intra-column \(\pi\)-stacking spacing, suggesting a 3\textsubscript{1} helical structure. In contrast, such projections in compound \textbf{S2}'s pattern have d-
spacing of 0.873 nm which is 2.50 times as that of its own π-stacking spacing. Moreover, there are weak diffractions at small angle with d-spacing of 1.85 nm around the meridional axis. Thus, it is likely that despite of sharing the same 2D lattice of columns and similar π-stacking spacing with S3, compound S2 has a 5\(_1\) helical structure with a rotation angle of 72° between two neighboring PEI units. As suggested by the theoretical calculation, 72° is even more favorable than 60° due to the larger value of transfer integral.\(^3\)

![Figure 4.4.1.](image)

(a) Room temperature 1D XRD pattern of S2. (c) Room temperature 1D XRD pattern of S2.
pattern of S3. Insets show the indexed weak small-angle diffractions. The peak marked “Si” corresponds to the diffraction from crystalline silicon powder that was added as the calibration standard. (b) Aligned 2-D XRD pattern of S2 at room temperature (d) Aligned 2-D XRD pattern of S3 at room temperature. Samples were melted into isotropic liquid state before experiment to remove thermal history. Shearing direction is pointing up as marked by the arrow.

Table 4.4.1. Cell parameters of DCLC phase of S2 and S3

<table>
<thead>
<tr>
<th>Compounds</th>
<th>α (β = γ = 90 °)</th>
<th>a=b</th>
<th>c</th>
</tr>
</thead>
<tbody>
<tr>
<td>S2</td>
<td>60 °</td>
<td>1.79 nm</td>
<td>0.349 nm</td>
</tr>
<tr>
<td>S3</td>
<td>60 °</td>
<td>1.86 nm</td>
<td>0.343 nm</td>
</tr>
</tbody>
</table>

Compounds S1 or S4 exhibits complex phase behaviors. To investigate reasons behind those phases developed through different approaches, XRD experiments were carried out and summarized in Figure 4.4.3. Samples of S1 and S4 prepared through evaporation of solvent were crystallized and thus produced large number of sharp diffractions covering the entire small to wide angle regions. In contrast, samples prepared through cooling from liquid states are amorphous, generating only diffused small angle scatterings. Therefore, we concluded that compounds S1 and S4 have difficulty to effectively arrange their side chains in order to form ordered structures. However, reasons for ineffective packing may be different for two compounds. Side chains adopt a symmetrical shape in S1 and thus uniform distribution of the alkyl moieties could be expected around the close periphery of the π-units aggregates. The short chain length should be responsible for the formation of amorphous phase. A LC phase destabilization could be noticed by comparing the clearing points of compounds S2 and S3.
They generally have the same spacer length and symmetrical design of the branched side chains. However, the clearing point of S2 becomes lower as the chain length is decreased. This observation implies a decreased LC phase stability. On the other hand, despite of having same number of atoms (or total length) in their side chains, S4 behaves very differently from S2. The difference should be attributed to the structure of S4’s swallow side chain which features a butyl-group and a much shorter ethyl-group on the branching site. It is likely that this asymmetrical swallow tail design is intrinsically troublesome to the molecular packing.
Figure 4.4.3. (a) Room temperature 1D XRD pattern of solution cast sample of S1. (c) Room temperature 1D XRD pattern of solution cast sample of S4. (e) Room temperature 1D XRD pattern of S1 prepared through cooling from liquid state. (g) Room temperature 1D XRD pattern of S4 prepared through cooling from liquid state. The peak marked “Si” corresponds to the diffraction from crystalline silicon powder that was added as the calibration standard. (b) Aligned 2D XRD pattern of solution cast sample of S1 at room temperature. (d) Aligned 2D XRD pattern of solution cast sample of S4 at room temperature. (f) Aligned room temperature 2D XRD pattern of S1 prepared through cooling from liquid state. (h) Aligned room temperature 2D XRD
pattern of S4 prepared through cooling from liquid state.

4.5. Conclusion

PEI derivatives with branched aliphatic substitutions have been designed and synthesized. Enantiotropic DCLC phases were identified with compound S2 and S3. None of four compounds crystallize quickly. Compound S3 has a wide LC phase temperature range (from -50 °C to 210 °C) which is suitable for most electronic applications. The advantageous 120 ° (or the supplement 60 °) and 72 ° rotation angle were identified with S2 and S3, respectively. Both samples are easy to form homeotropic alignment on the ordinary or ITO coated glass surface with essentially no requirement of fabrication technique. The compound is well soluble in various organic solvent but not in water. Combining high π-stacking order, good chemical and thermal stability, macroscopic molecular orientation and good processability, enantiotropic DCLC S2 and S3 are promising candidates as organic charge transport materials or electron acceptors in photovoltaic cells.

4.6. Experimental section

Instrumental analysis and characterization

\(^1\)H NMR spectra were recorded on a Varian 600 MHz NMR spectrometer, with deuterated chloroform (CDCl\(_3\)) as solvent at 25 \(^\circ\)C. The chemical shifts were reported using chloroform as the internal standard. The NMR graphs and data were collected by using Spinworks 3 software. The peak at 7.26 ppm with two satellite peaks belongs to CHCl\(_3\) residue and the peak at 1.58 ppm belongs to H\(_2\)O.

All XRD measurements were performed at RT on a Bruker Nanostar instrument with a
Cu $K_{\alpha}$ source. A VÅNTEC 2000 2D detector and an image plate were used as small and wide angle detectors, respectively. Powder LC samples for XRD studies were prepared by first heating up to isotropic liquid state, then cooling down to RT. Aligned LC samples were obtained by mechanical shearing of powder LC samples. The crystallized samples were prepared by allowing aligned LC samples to crystallize over hours to days. The typical X-ray exposure time is 8 hours for an oriented crystalline sample.

Polarized light microscopy picture shown in Figure 1 was taken from a Leica DM LB2 microscope equipped with a Leica DGC 320 camera and a Mettler Toledo FP82HT hotstage (controlled by a Mettler Toledo FP90 central processor). Samples were heated beyond their clearing points and cooled down slowly at approximately 0.03 °C/min ramp rate to temperature closely below phase transition.

DSC experiments were performed on a Perkin-Elmer PYRIS Diamond differential scanning calorimeter. Transition temperatures were determined using onset temperatures and were calibrated using standard material (indium).

**Materials and Synthesis**

All reagents were used as received. Diethyl malonate (98%), 1-bromobutane (98%), 2-ethylbutan-1-ol (99%), 2-ethylhexan-1-ol (98%), 2-propylpentan-1-ol (98%), dimethyl sulfoxide (98%), 4-Toluenesulfonyl chloride (99%) were purchased from Sigma Aldrich.

The swallow tail 2-butylhexan-1-ol was synthesized partly according to a literature procedure.$^3$

**Diethyl 2,2-dibutylmalonate**

The reaction system was protected by Argon during entire operation. Caution was taken to prevent moisture from coming inside the reaction container. Into a 500 ml round-bottomed
flask were charged with 16.007 g (100 mmol) diethyl malonate. Cool the flask and liquid inside to 0 °C by an ice-water bath. Into the liquid was added 15.700 g (220 mmol) sodium ethoxide pre-dissolved in 250 ml ethanol (200 proof, freshly distilled with sodium). The solution was then cooled to 0 °C and stir for 20 minutes. Subsequently, 30.30 g (220 mmol) 1-bromobutane was added into the solution dropwise. The mixture was then refluxed for 19 hours. Upon completion of reaction, the mixture was evaporated on a rotary evaporator under vacuum and the high boiling point liquid inside the flask was dissolved in distilled water. The water solution was then extracted by 150 ml hexane for 3 times. The organic phase was combined and evaporated to yield the crude product of diethyl 2,2-dibutylmalonate as an oil-like liquid which was directly used in the following synthetic step assuming 100% yield.

2,2-dibutylmalonoic acid

To the 500 ml round bottomed flask which contained the crude product of diethyl 2,2-dibutylmalonate were charged with 42.20 g (640 mmol) potassium hydroxide, 108 ml of ethanol (95%) and 72 ml distilled water. The solution was then heated to 70 °C for 20 hours. The mixture was later cooled to RT and acidified to pH = 2 with hydrochloric acid (1M). The solvent was removed by rotary evaporator under vacuum. The residue was extracted by 150 ml ethyl acetate for 4 times. The organic phase was combined and washed with brine, anhydrous magnesium sulfate. The solution was then filtered and evaporated on a rotary evaporator under vacuum. The resulting oil was wash with brine again and precipitated in cold hexane. The light yellow precipitate was recrystallized with the mixture of ethyl acetate and hexane. The relatively pure product which is white needle-like crystal was directly used in the next step of reaction without further purification. The yield was determined to be ca. 9.0 g (42%, with respect to the starting material, diethyl malonate)
2-butylhexanoic acid

To a 10 mL round bottomed flask was charged with 3.0 g of 2,2-dibutylmalonoic acid. Purged with Argon, the solid was heated to 170 °C with stirring for 45 minutes. The product is a clear colorless liquid which weighed 2.17 g (99%) and was directly taken to the next step of reaction without further purification.

2-butylhexan-1-ol

To a 250 mL round bottomed flask were charged with 3.18 g (51.2 mmol) LiAlH₄ and 20 mL anhydrous THF. The solution was then cooled to 0 °C. Under the protection of Argon, 2.17 g (12.8 mmol) 2-butylhexanoic acid pre-dissolved in 20 mL anhydrous THF was added dropwise into the solution. The reaction mixture was stirred at 0 °C for another 4 hours and later quenched by adding 10 mL ethyl acetate. THF was removed by evaporation on a rotary evaporator under reduced pressure. Subsequently, to the residue was added 10 mL distilled water. The resulting gel was vigorously extracted by 50 mL ethyl acetate for 4 times. The organic phase was combined and washed with brine and dried over anhydrous magnesium sulfate. After filtration, the ethyl acetate solution was evaporated on a rotary evaporator under vacuum to yield a light yellow oil-like clear liquid. The alcohol could be easily purified by performing the column chromatography. The yield is calculated to be 1.685 g (85%).

2-hexyloctanyl 4-methylbenzenesulfonate

The target compound was synthesized according to a literature procedure.⁴ To a 50 mL round-bottomed flask were charged with 1.685 g (10.66 mmol) 2-butylhexan-1-ol, 2.700 g (26.66 mmol) triethylamine, 0.158 g (1.60 mmol) trimethylamine hydrochloride and 11 mL dichloromethane. Then the mixture was cooled and stirred in an ice-water bath for 20 minutes. Afterwards, 1.924 g (10.09 mmol) 4-methylbenzenesulfonyl chloride was dissolved in 11 mL
dichloromethane and the solution was added in a dropwise fashion into the reaction flask using a constant pressure funnel. Care was taken to maintain the temperature of the ice-water bath at 0 °C during the reaction. The reaction progress was monitored by thin layer chromatography. The reaction was ended when 4-methylbenzenesulfonyl chloride was fully consumed and it took approximately 90 minutes. Upon the completion of reaction, 6.5 g (56 mmol) phosphoric acid and 10 ml water were added into the reaction mixture. The mixture was stirred for 15 minutes. Then the suspension was extracted with dichloromethane. The organic phase was later washed with brine, dried over anhydrous magnesium sulfate and evaporated on a rotary evaporator. The liquid residue was purified by silica column chromatography with chloroform as the eluent. The yield of 2-butylhexanyl 4-methylbenzenesulfonate was calculated to be 2.950 g (89%), as a colorless liquid.

**General procedure of S1, S2, S3 and S4**

Into a 10 ml Schelenk flask were added 196 mg (0.5 mmol) PTMIMA (391.33 g/mol), 696 mg (1.475 mmol) tetrabutylammonium hydroxide (55% w.t. water solution) (259.47 g/mol) and 5 ml DMSO. To allow a complete dissolving of the PTMIMA, the mixture was heated to 40 °C for 3 hours under nitrogen protection. Subsequently, 2 mmol of the corresponding alkyl tosylate was added into the purple pink solution. The solution was then heated to 60 °C for 48 hours under nitrogen protection and shielded from light. After cooling down to RT, the reaction mixture was transferred to a 125 ml separatory funnel and the reaction vessel was rinsed by a small amount of chloroform which was later combined with the mixture into the funnel. Along the inner wall of the funnel was added slowly with a pipette 50 ml of distilled water and then swirled gently to allow the DMSO to diffuse into the water layer. Repeat the washing process for an additional 2 times. The leftover organic layer was purified through column chromatography.
using chloroform as eluent to yield pure red solids.

4.7. References


4. (a) Yoshida, Y.; Shimonishi, K.; Sakakura, Y.; Okada, S.; Aso, N.; Tanabe, Y., Facile and practical methods for the sulfonylation of alcohols using Ts(Ms)Cl and Me₂N(CH₂)₈NMe₂ as