Synthesis and Characterization of Novel Discotic Liquid Crystal Porphyrins for Organic Photovoltaics

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by

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<th>Description</th>
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<tbody>
<tr>
<td>AcOH</td>
<td>acetic acid</td>
</tr>
<tr>
<td>CH$_2$Cl$_2$</td>
<td>methylene chloride</td>
</tr>
<tr>
<td>Col$_h$</td>
<td>hexagonal columnar liquid crystal phase</td>
</tr>
<tr>
<td>Col$_{ho}$</td>
<td>more ordered hexagonal columnar liquid crystal phase</td>
</tr>
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<td>Cr</td>
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<tr>
<td>C$_{60}$</td>
<td>(C$_{60}$-I$_h$)[5,6]fullerene</td>
</tr>
<tr>
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</tr>
<tr>
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<td>IR</td>
<td>Infrared</td>
</tr>
<tr>
<td>ITO</td>
<td>indium tin oxide</td>
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HCl  hydrochloric acid

$J$  coupling constant

KI  potassium iodide

l  liter

m  multiplet

M  mole per liter

MALDI  matrix assisted laser desorption/ionization

MeOH  methanol

min  minute

mmol  milli mole

m.p.  melting point

Ms  mass

LC  liquid crystal

NaH  sodium hydride

NMR  nuclear magnetic resonance

OPV  organic photovoltaic

PCBM  [6,6]-phenyl C$_{61}$ butyric acid methyl ester

ppm  part per million

POM  polarized optical microscope

PV  photovoltaic

p-TsOH  p-toluenesulfonic acid

SAXD  small angle X-ray diffraction
<table>
<thead>
<tr>
<th>Symbol</th>
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<td>s</td>
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<td>t</td>
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Chapter 1

Introduction

1.1 Background of Photovoltaics

The sun provides about 100,000 terawatts (TW) of power to the Earth, which is about 10,000 times greater than the world’s present energy consumption (13 TW). If 0.1% of the Earth’s surface was able to harness this solar energy with a conversion efficiency of 10%, human’s needs for energy could be met completely. Currently photovoltaic (PV) cells are being used to convert this huge amount of energy into electricity. Fig. 1.1 shows the photovoltaic peak power installed annually from 1988 to 2003. If this trend continues, by 2010, the module output production will be quadruple, reaching 6 GW (gigawatts) and by 2030, it will reach 200 GW.\(^1\) However, 200 GW by 2030 is still not enough to make a major impact because the world’s energy consumption will by then approach 20 TW. Considering the energy crisis with the increasing price of oil and crude material, the energy dependence on solar power could be much higher. Therefore, the need for better, more efficient PV cells will become crucial as time progresses.
Conventional PV cells are based on silicon layers. Fig. 1.2 shows a simple diagram of the fundamentals of a conventional PV cell. The bottom and the top layers are made of a p-doped (extra holes) and an n-doped (extra electrons) silicon. Close contact of these two materials results charge carriers in each layer attracting and eliminating each other, thus allowing a flow of electricity. When a light is shined on the surface of the cell (yellow arrows in Fig. 1.2), photons are absorbed. The absorbed energy from photons promotes electrons from the valence band (covalent bond state) to the conduction band (delocalized state) of the silicon and thus creates electron-hole pairs. Charge diffusion then occurs from the n-type side of the junction (high electron concentration) to the p-type side of junction (low electron concentration).
This kind of silicon p-n junction cell was developed in 1954 with a 6% efficiency, commercialized in the 1960s and applied to the space program.\textsuperscript{3,4,5} So far silicon photovoltaic materials account for the vast majority of photovoltaic cells. Although the efficiency of this kind of PV cells can reach about 30%, they are significantly lowered during commercialization due to scale up effects. Also, from the cost perspective, this type of cell is highly dependent on the supply of silicon. The silicon for today’s PV cells originates mainly from waste produced by the chip industry. But the cost of solar-grade silicon jumped from $9 per kilogram in year 2000 to $60 per kilogram in 2005. With the increasing demand in the market and the slower increase in supply, the price is expected to continually rise. Compared with the price of traditionally generated electricity, $0.05 per kWh, the cost for the best PV systems installed at the best sites is in the range of $0.25-0.65 per kWh.\textsuperscript{6} So, research on this conventional PV cell module cannot only be focused on the successful conversion of solar energy, but must also provide a competitive alternative to consumer demand.
Since the 1970s, a second generation of thin film PV cells has emerged. The main examples of this type of PV cells include amorphous Si, thin-film Si, CuIn(Ga)Se₂, CdTe, light-absorbing dyes (DSSC) and organic materials (molecular and polymeric). The amorphous Si and thin-film Si is less expensive than crystalline silicon cells but their lower efficiency makes their cost similar on a per peak-watt basis. The CuIn(Ga)Se and CdTe have a better conversion efficiency (15-20% from the best laboratory result), but they are harder to commercialize because of the scarcity of indium, tellurium, selenium and the high toxicity of cadmium. Although a much smaller amount of these materials is needed, they are still too expensive compared with silicon. The DSSC allows flexible use of materials and has potential for lower costs than those used for bulk solar cells. However, the dyes in these cells suffer from degradation under heat and UV light. A
particularly promising second generation thin film PV cell is based on organic materials.\textsuperscript{9} The cheap cost and high efficiency potential make this area of PVs worth looking into.

\subsection*{1.2 Organic Photovoltaic Materials}

The development of organic photovoltaic (OPV) material as alternatives has drawn more and more attention. The OPV technology would hold a promise for cost reduction since the OPV materials are potentially cheap, easy to process and capable of being deposited on flexible substrates and bent, whereas their inorganic competitors, e.g. crystalline silicon, would crack.\textsuperscript{10}

Unlike inorganic semiconductors, in which free charge carriers are generated immediately after the absorption of light, the excitons created in OPVs by photon absorption need to be dissociated to generate current. So, it’s essential to have two components: electron donor and electron acceptor for the charge separation. Fullerene and its derivatives are widely used as electron acceptors for OPV devices because of their strong electron affinity.\textsuperscript{11,12} Fullerene has long been found to have outstanding electron acceptor features. Their usage in solar cells was not well explored until their production in milligram quantities was achieved. C\textsubscript{60} is the most common fullerene molecule and the smallest among the fullerene family. Because of the fast development of C\textsubscript{60} chemistry, nearly any functional group can be covalently bonded to the core. This even gives a chance to link an electron donating polymeric group to C\textsubscript{60}. One of the well-known C\textsubscript{60} fullerene derivative is [6,6]-phenyl C\textsubscript{61} butyric acid methyl ester (PCBM) (Fig. 1.3). Compared to C\textsubscript{60}, PCBM has much better solubility in organic solvent.
The blend of semiconducting $\pi$-conjugated organic polymers, such as $p$-phenylenevinylene (PPVs) and polythiophenes (PTs), with fullerene affords new types of plastic solar cells with relatively moderate conversion efficiency compared with silicon-based solar cells.\textsuperscript{13} The advantage of these materials is that the electron transfer between the electron-donating polymer and the electron-accepting fullerenes occurs with ultrafast dynamics and high quantum efficiency. The disadvantage of this approach is the tendency of $C_{60}$ to phase separate from the polymer and to crystallize. This brings up problems for its solubility in conjugated polymer matrices.\textsuperscript{14} This approach opens up a lot of possibility to modify the blends with a large pool of electron donating polymer or oligomer and a variety of different modification of fullerenes, potentially increasing conversion efficiency.\textsuperscript{15,16}

It is well-established that the OPV materials in highly efficient PV cells are critically dependent on the supramolecular arrangement of the blend made from the electron donor and electron acceptor components. Compared with donor and acceptor bilayer PV cells, a
blend can offer a much larger interface between donor and acceptor leading to an efficient dissociation of excitons in the supramolecular arrangement.\textsuperscript{17}

Pasimeni et al.\textsuperscript{18} studied the blend consisting of sexithiophene and fullerene derivatives in the solid phase, and found that charge separation generated by photo-induced electron transfer in fullerenes has a much longer lifetime than covalently linked dyads. Hadziioannou et al.\textsuperscript{19} studied the blend between poly(phenylenevinylene)s (PPV) and fullerene, and demonstrated that finger-shaped interpenetrating morphologies for organic photovoltaic devices have great potential. Andreev et al.\textsuperscript{16} have obtained single layers and bilayers of p-sexiphenyl (PSP) and C$_{60}$ grown by hot wall epitaxy (HWE). This technology allows growing epitaxy layers close to thermodynamic equilibrium. As a result, the organic molecules can find the suitable arrangement before being incorporated into the crystal lattice, resulting in highly ordered structures of the deposited layers. Examples of conjugated oligomers used for OPV materials are shown below in Fig. 1.4.

![Conjugated oligomers](image)

**Fig. 1.4** Examples of conjugated oligomers used in blends with C$_{60}$. 
1.3 Photoconductivity of Discotic LCs

Among the OPV materials, LCs are being recognized as a new type of organic semiconductors. One of the main reasons is that some discotic LCs exhibit very high charge mobility which is thousands times higher than amorphous organic semiconductors. In 1993, Haarer et al. discovered the fast electronic conduction in a discotic LC phase of hexapentyloxytriphenylene (HPT), which attracted great attention at that time.20

Extensive studies on the electrical properties of LCs go back to the late 1960s. Heilmeier first measured the ionic mobility of p-azoxyanisole in 1968. In the 1970s, the ionic mobility was determined in various LCs, and in the 1980s the major research had moved from calamitic LCs to discotic LCs which were discovered by Chandrasekahr in 1977.23 Haarer et al. finally proved that fast electronic conduction exists in a non-doped triphenylene derivative; using the time-of-flight (TOF) technique they estimated its mobility to be 10⁻³ cm²/Vs.20
Fig. 1.5 Example of some high mobility discotic liquid crystals.
Photoconducting liquid crystalline materials can be classified into three categories. One is discotic LCs such as triphenylenes, phthalocyanines, perylenes and hexabenzocoronenes as shown in Fig. 1.5, which can self-organize into columnar structure. The second one is smectic LCs in which the electronic conduction takes place within the two dimensional smectic layers. Typical examples of such smectic LCs are 2-phenyl-substituted benzothiazoles, naphthalenes, terthiophenes and benzothieno-benzothiophenes. The third one is polymeric LCs such as polyfluorenes and polyacrylates having a 2-phenynaphthalene moiety (Fig. 1.6). Polyfluorenes are linearly conjugated main chain polymers exhibiting nematic and nematic glassy phases and the polyacrylate having a 2-phenynaphthalene moiety is a polymer with smectic phases. They all exhibit fast electronic conduction with high mobility.

There are three dominant factors in deciding the magnitude of the charge carrier mobility for the discotic LCs in the first category: the degree of order within the column, the size of the aromatic core and the extent of electronic overlap between adjacent molecules. The columnar superstructures of the discotic LCs allow the charge carriers to achieve transport along the column. Thus, the key issue to have high electron mobility includes both the structure of \(\pi-\pi\) conjugated system at the aromatic core and the homeotropic alignment of the columnar structure. Because of their high viscosity, discotic LCs are hard to align perpendicular to the substrate. As more and more research emerges, it is found that small sized aromatic cores of discotic systems can spontaneously align homeotropically when cooling from the isotropic phase while big core systems such as hexa-peri-hexabenzocoronene (HBC) are hard to homeotropically align and need
special coating, e.g. pre-oriented polytetrafluoroethylene (PTFE) applied to the substrate. Yet bigger core sizes tend to have higher carrier mobility.\textsuperscript{26,27} Porphyrins, included in the first type, as molecules with a large core, will be focused on for this work.

![Chemical structures](image)

**Fig. 1.6** High mobility smectic and polymeric liquid crystals.

### 1.4 Brief Introduction to Porphyrins for PV application

Porphyrins all share a similar core structure of porphine. Porphyrins are also found in nature such as in chlorophyll which is thought to be the best photoreceptor in nature (Fig. 1.7). Chlorophyll can strongly absorb light and transfer that light energy into photosystems which is vital to photosynthesis. Porphyrins have intense absorption in the
near-ultraviolet and visible regions giving them deep colors. For this reason, they have been selected as photosensitizers in photovoltaic materials.

Porphyrin sometimes is called free base if there is no metal inserted into its core. When a metal atom is bonded to the central nitrogen atoms of a porphyrin, we call this porphyrin derivative a “metalloporphyrin”. And the process of producing the metalloporphyrin is metalation. As we can see that chlorophyll is a magnesium-metalated porphyrin.

![Chemical structure of porphine and chlorophyll.](image)

**Fig. 1.7** Chemical structure of porphine and chlorophyll.

A LC porphyrin was first synthesized in 1980. Using LCs, especially those which exhibit a columnar phase, has the advantage that they could be homeotropically aligned i.e. the columns formed by intermolecular strong π-π self assembly perpendicular to the surface.
Porphyrin has a very close association with fullerene in photovoltaic materials. This close association was first recognized in molecular packing of a crystal structure containing a covalent fullerene-porphyrin conjugate. The distance between the center of the porphyrin and fullerene was measured as 2.75 Å, which is shorter than the separation of common $\pi-\pi$ interactions.\textsuperscript{29} This means the porphyrin has a stronger interaction with fullerene than other electron donators like arenes. As a result, porphyrin could have a better charge separation with fullerene in photovoltaic systems.

For such porphyrin-fullerene blend materials, if the defects along the columns are minimized, we expect higher charge carrier mobility in terms of highly ordered columns arranged perpendicular to the surface. Such homeotropic alignment favors charge carriers transport along the columns which is referential for the PV cell as shown below (Fig. 1.8).\textsuperscript{30,31}
Some work on porphyrins as photovoltaic materials has already been reported. Bard’s group discovered pressure-induced insulator-conductor transition in a photoconducting organic LC film. They also found that solid-state packing of the alkylated porphyrins influences the attainable photoconductivity and the efficiency of photocurrent production when these materials are formulated as thin solid films in ITO sandwich cells. Unfortunately, due to the extremely difficult synthesis, research on their applications did not make good progress. Furthermore, there was no evidence to indicate whether the LC porphyrins can be homeotropically aligned or not.

1.5 Alignment of Discotic Liquid Crystals

LCs can respond easily to external stimuli and their alignment can be manipulated by external fields and surface effects. Thus, discotic LCs are supposed to carry charges and
excitons more efficiently than conventional conjugated polymers and they are viewed as a new generation of organic semiconductors.34

There are two typical alignments of discotic LCs, namely homogeneous and homeotropic alignments. Homogeneous alignment in which the columns are parallel to the electrode surface has potential applications such as organic thin-film transistors. As mentioned above, the homeotropic alignment of photoconducting discotic LCs is crucial for achieving high conductivity for the PV application and organic light emitting diodes. However, most of the alignments reported to date contain domain boundaries and disclinations which prohibit the carrier transport. It’s a challenge to achieve perfect homeotropic alignment over a large area in thin films.

Although alignment of rod-like LCs on surfaces or in LC cells is a well-established technology, few of the alignment methods developed for these LCs can affect the alignment of the discotic LCs. Thus, alignments obtained by utilizing interfacial forces or by applying external fields for rod-like LCs are hardly to apply to discotic LCs. One of the methods that can align the discotic LCs is using a magnetic field. The alignment usually takes place at the transition temperature from isotropic or less ordered discotic nematic phase to the columnar phase when the viscosity is small. The more viscous the discotic LCs material is, the larger the magnetic field that is needed. Surface anchoring has been successfully utilized in LC displays in which rod-like LCs are predominantly aligned by interactions with specially treated or prepared surfaces. However, alignment of discotic LCs on a surface appears to depend very little on the surface treatment but is more likely a property of the discotic LC material itself. Highly viscous discotic
columnar mesophases do not easily form a monodomain and prefer a homogeneous alignment rather than homeotropic alignment. So it is not easy to achieve the advantageous homeotropic alignment of discotic LC porphyrins although LC porphyrins as promising organic electronic materials had been demonstrated.\textsuperscript{35}

Enhancing this kind of alignment would greatly improve the efficiency of the photovoltaic cells. A breakthrough in alignment tendency will very possibly lead to a breakthrough in solar energy conversion. This dissertation focuses on the improvement of the homeotropic nature of porphyrin through modification of the porphyrin molecule itself.

1.6 Approach

In order to make the discotic LC with more efficient absorption of sunlight, porphyrin as a “disc” would be its best functional building block since it is the basic structure of the best photoreceptor chlorophyll in nature. Porphyrins have many desirable features such as a highly conjugated plane, high stability, intense absorption of sunlight, and a small gap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy level.

The first porphyrin based liquid crystal with an unsymmetrical structure and an LC phase over a range of 0.1 °C only on cooling was synthesized by Goodby in 1980, but no attempt was made to measure its electrical or optical physical properties.\textsuperscript{36} Over the last two decades, the most impressive example of liquid crystalline porphyrin towards potential organic electronic material was reported by Bard et al.\textsuperscript{32,37,38,39} Unfortunately, no further research was made due to the extremely difficulty for its re-synthesis even in
the same lab. Much synthetic effort had been taken to provide its analogues with relatively easy synthesis, but none of the derivatives shows a stable liquid crystalline phase.\textsuperscript{33}

On the other hand, currently widely used OPV materials suffer from the scattering of electron/exciton between small crystal grain boundaries in which random arrangement of molecules results in poor charge mobility. As described above, a challenge for OPV, with the possibility of very significant cost reduction, is to make them in a desired macroscopic order to improve charge transportation. The discotic LCs, which can be homeotropically aligned, would be the desirable candidate to meet the challenge since they can form ordered nanostructure at macroscopic scale for photovoltaic application. This however is not an easy work, because discotic LCs with big $\pi$ conjugated “disc” have a higher order of molecular orientation and thus tend to show a viscosity much higher than the rod-shaped LCs such as nematic and smectic phase. For this reason, discotic LCs are very difficult to achieve their homeotropic alignment although the alignment technology of rod-shaped LCs is well established in liquid crystal display industry.\textsuperscript{40}

Though discotic LCs have high viscosity which prohibits them to align perpendicular to the substrate, when the material goes into the mesophase, it is relatively easier to align homeotropically from the isotropic state. For the porphyrins previously investigated from other groups, the homeotropic alignment was destroyed significantly at the solid crystal state.\textsuperscript{41} The surface affinity to the substrate was not enough to maintain the alignment.
Thus, we want to design a molecular which is relatively easy to make but has a low viscosity at its mesophase temperature.

To meet these challenges, we designed the porphyrin core as the rigid part and attached moderate flexible alkyl side chains to the core to introduce the fluidity. Four phenyl rings were attached to the porphyrin core and twelve symmetrical alkyl side chains were connected to the benzoic acid via esterfication to get the target compound. We expected the designed molecules could show discotic LC phase by combining rigid and flexible parts.

To further improve the alignment of the LC porphyrins, fluorine atoms were introduced. Compared with alkyl chains, perfluorinated alkyl chains have long been found to be more rigid, more linear and less miscible in organic solvent than the corresponding perhydrogenated alkyl chains due to their extremely low surface energy. 42 This is well known as the fluorophobic effect. Previously, it has been shown that chain perfluorination of a small discotic system, i.e. triphenylenes, supports columnar packing.43 There appears no report on the success that introducing perfluoroalkyl chains into large conjugated discotic molecule leads a strong tendency for a homeotropic alignment, which are practically important for their possible applications, although large conjugated perfluoroalkylated discotic LC such as hexabenzocoronenes were synthesized. As a result, in order to enlarge the surface affinity and making the homeotropic alignment easier to achieve, we modified the side chains of the porphyrin systems prepared in Chapter 2 by introducing fluorine atoms at the terminal chains.
Chlorophyll, the best photoreceptor in nature, is magnesium inserted porphyrin complex. Thus, lots of research has been done to resemble chlorophyll to have its light-harvesting and electron-transfer properties. In order to investigate how metal can affect the charge transport along the column and the electronic properties, we inserted Zn, Cu and Mg to all the synthesized target porphyrins. We want to see if there is any phase change or absorption as well as photoemission change occur.

In addition to improving homeotropic alignment, the effect of introducing chirality into columnar LC systems was studied for potential application in nonlinear optics as part of this study. Porphyrins with a chiral moiety were synthesized and characterized. Based on previous experiences, porphyrins synthesized via intermediate porphyrin core with moderate functional chains, show columnar LC phases. Thus, in the simplest way, we introduce the chiral moiety into the chains in order to obtain the supramolecular chirality. With the introducing of chirality, we want to see if the designed molecules have helical structure in columnar phase.
Chapter 2

Non-fluorinated Liquid Crystal Porphyrins

Part of this chapter is also available in

“Self-assembly of porphyrin and fullerene supramolecular complex into highly ordered nanostructure by simple thermal annealing” X. Zhou, S. Kang, S. Kumar, S. Cheng, Q. Li Chemistry of Material 2008, 20, 3551.


2.1 Molecular Design of Non-fluorinated Porphyrins

2.1.1 Some Previously Reported Porphyrins

Bard’s group was very active in the liquid crystal porphyrin field. For example, as early as 1989, they synthesized 2,3,7,8,12,13,17,18-octakis(β-hydroxyethyl)porphyrin (octaethanolporphyrin) and its octaalkyl ether derivatives. The octakis(alkoxyethyl)porphyrins (P1) they synthesized exhibit a discotic liquid crystalline phase. Unfortunately their synthesis took about 13 steps and the yield was extremely low,
making research on this kind of porphyrin difficult to continue. The same group managed to explore an alternative to this material\textsuperscript{33}; they synthesized two different substituted porphyrins (\textbf{P2} and \textbf{P3}) utilizing two different synthetic routes. Unfortunately, these two derivatives have not shown a stable LC phase. Later on, Monobe et al. provided another example of modified porphyrin core (\textbf{P4}).\textsuperscript{44} This analogue was reported to have a discotic mesophase.
2.1.2 Design of Target Porphyrins

Comparing the previous examples, although there is not a clear trend, there do seem to be some factors which play a critical role between molecular structure and LC properties. First of all, the length and the abundance of alkyl chains appear to be very important. If
the chain length is too short, it could lose its LC phase. But if the chain length is too long, e.g. P2, it could be too flexible and the phase becomes disordered. Also, it might be necessary to introduce oxygen, as in compound P3, to help displacing the chain from the core, because overly long chains could well surround each other and destroy the π-stacking of the molecules. Another factor in impacting a LC phase could be the metal with which porphyrin is complexed. For example, nickel complex P4 exhibits a LC phase while zinc complexes P2 and P3 do not exhibit a LC phase.

In deciding the exact alkyl length, preliminary studies by L. Li\textsuperscript{45} in our group were looked into. Moderately long chain lengths of 13 and 15 were selected based on her work.

![Fig. 2.2 Molecular structure of benzene-hexa-n-alkanoate (R = C\textsubscript{n}H\textsubscript{2n+1}).](image)

Additionally, some discotic LCs have been shown to undergo an odd-even effect with respect to the number of carbon atoms in a side chain of a disc-like molecule. Asahinda et al., have observed an odd-even effect in the cumulative transition entropies of the compound shown in Fig. 2.2.\textsuperscript{46} The molar entropies exhibited a peculiar pairing phenomenon between the odd and even chains. So it’s reasonable to speculate that the odd-even effect could also exist in LC porphyrins affecting the phase transitions. This was taken into consideration in the final steps of the synthesis where an odd chain length was chosen for the first porphyrins synthesized in this work.
2.2 Synthesis

2.2.1 General Synthesis of Porphyrin

All porphyrins were synthesized starting from pyrroles. The 5,10,15,20-mesotetrakis(aryl)porphyrin (TPP) is made by refluxing pyrrole with benzaldehyde in propionic acid for 30 minutes. The resulting mixture was filtered, washed with ethanol and propionic acid, and dried to give a solid product (Fig. 2.3). The mechanism of this reaction involves the electrophilic α-substitution of pyrrole by acid-catalyzed oligomerization and cyclization between four pyrrole units.

![Synthesis of 5,10,15,20-mesotetrakis(aryl)porphyrin.](image)

For the ease of synthesis, the phenol was attached to the porphyrin core as a key intermediate A (Fig. 2.4) which was synthesized by Li. This porphyrin intermediate A was kept intact for all the target porphyrins in this dissertation.

Two target porphyrins with odd numbered long alkyl side chain tails were successfully synthesized. To study the odd-even effects of side chains on the porphyrin tail, these targets were chosen to compare with porphyrin with even alkyl chains previously
synthesized in our group, as well as for furthering the investigation of the properties of this kind of photovoltaic material. The synthesis follows the steps in L. Li’s thesis.45

To complete the final structure of the target molecule, benzoic acid intermediates must also be prepared before reacting with the porphyrin intermediate A. The benzoic acids were prepared in a two step process and then used as the other intermediates in the final reaction to obtain the target molecules.

![Structure of the intermediate A: 5,10,15,20-tetra(p-hydroxy phenyl) porphyrin.](image)

**Fig. 2.4** Structure of the intermediate A: 5,10,15,20-tetra(p-hydroxy phenyl) porphyrin.

### 2.2.2 Synthesis of Benzoates and Their Corresponding Benzoic Acids

The procedure is pretty straightforward. It started from the commercially available methyl tris-3,4,5-hydroxy benzoate and alkyl bromide by Williamson ether formation reaction. The mixture of tris-3,4,5-hydroxy benzoate and alkyl bromide were stirred in DMF (dimethylformamide) with potassium carbonate at a temperature of 70 °C for about 18 hours (Scheme 2.1). If the reaction time is too short, monosubstituted and
disubstituted byproducts form as the major product due to incomplete substitution (Scheme 2.2).

Scheme 2.1 Synthetic scheme of intermediate benzoate 1 and benzoic acid 2.

The desired benzoic acids 2a and 2b were obtained from hydrolysis of the corresponding esters 1a and 1b at 70 °C under strongly basic conditions. After 2 hours, aqueous HCl was added to precipitate the product. Simple filtration of the solid typically led to high yields around 90%.

Scheme 2.2 Byproducts from the ether formation reaction.

2.2.3 Synthesis of Target Porphyrins
The final step was carried out between the intermediate 5,10,15,20-tetra(p-hydroxy phenyl) porphyrin and tris-alkoxy benzoic acid intermediate by the esterification under the condition of DCC (dicyclohexyl carbodiimide) and DMAP (4-dimethylaminopyridine) (Scheme 2.3). The target compounds were purified on silica gel by flash column chromatography in about 50% yield.
Scheme 2.3 Synthetic scheme of target porphyrins 3.
2.3 Thermal Behavior

In order to study the thermal behavior of these target porphyrin compounds, DSC (differential scanning calorimetry) and POM (polarized optical microscope) were used to characterize them. All DSC data was carried out at the rate of 5 °C/min if not otherwise specified. The transition temperatures from POM are uncorrected. The phase reported here *Col₉* (hexagonal columnar LC phase) and *Colho* (more ordered hexagonal columnar LC phase) are labeled based on X-ray results to be discussed later.

2.3.1 Differential Scanning Calorimetry of Compounds 3

DSC shows that for initial samples of all the compounds, there is always a large peak during the heating sequence that disappears on the repeated runs. Taking compound 3a as an example, a broad peak showed up at 70.44 °C with a large enthalpy (64.75 J/g) when heated at a rate of 5 °C/min during the first heating and disappeared at the second heating sequence (Fig. 2.5). This peak originates from the fact that, after a melt, the sample doesn’t return back to the original powder form, so the peak disappears on subsequent heating. Due to these reasons, it is typical to rely on the second cycle of heating and cooling for an indication of phase behavior.

Three clear transition peaks were observed for 3b during the cooling sequence in the second cycle. On cooling from isotropic, the first peak at 130.69 °C with 2.16 J/g latent heat is attributed to the transition from isotropic phase to *Col₉* phase. The second peak was observed at 104.87 °C with a slightly larger enthalpy of 5.82 J/g and corresponded to the phase transition from the *Col₉* phase to a more ordered *Colho* phase. With the enthalpy of 23.08 J/g, the third transition peak appeared at 1.98 °C. It is assumed that the
last peak comes from the transition between columnar LC phase and crystal phase, because of a much larger latent heat than the other two transitions. The thermograms of cooling sequences for compound 3b at different rates are shown in Fig. 2.6.

Fig. 2.5 DSC thermograms a) of the first cycle and b) of the second cycle at the rate of 5 °C/min for compound 3a (heating: dark blue line; cooling: pink line).
The heating and cooling rate cause a shift in the DSC transition temperature, because when the sample is cooled quickly, the material is unable to respond fast enough, and as a result, the temperature lags behind where it should be (Fig. 2.6). For compound 3b, it was found that during the first transition from isotropic to \( \text{Col}_h \), the temperature lags by 0.98 °C, in the 5 °C/min rate vs. the 1 °C/min rate. From \( \text{Col}_h \) to more ordered hexagonal phase \( \text{Col}_{ho} \), it is more lagged by 4.03 °C and is seen again in the transition from \( \text{Col}_{ho} \) to crystal phase with a 1.44 °C lag. It is also noticed that the lag for each transition is different and doesn’t seem to follow a trend. This might be attributed to the different thermal behaviors of each phase to phase transition.

![DSC thermogram of 3b at the rate of 5 °C/min (pink line) and 1 °C/min (dark blue line).](image)

**Fig. 2.6** DSC thermogram of 3b at the rate of 5 °C/min (pink line) and 1 °C/min (dark blue line).

To further understand the phase behavior in relation to chain length, a comparison of the compounds 3a (R=13) and 3b (R=15) with T12, T14 and T16 (R=12, 14, 16) from Li’s thesis were made. It is well known that the melting points of n-alkanes occur in a
zigzag manner with the increase of chain length and the even alkanes have relatively higher melting temperatures.\textsuperscript{48, 49, 50, 51} Investigation of this phenomenon shows that this is due to the differences in alkane chain packing of the even and odd number of alkanes.\textsuperscript{52, 53}

The phase transitions of these five compounds are summarized in Table 2.1. DSC shows that the isotropic temperatures decrease with the increase of alkyl chain length (Fig. 2.7). The tendency of the isotropic transition temperature is consistent and no zigzag curve was observed in either the temperatures or the latent heat. There appears to be no odd-even effect on the side chain of porphyrins. Though no odd-even effect was found, this study gives insight to the stabilization of the \textit{Colh} phase based on alkyl chain length. According to Li’s thesis, below the chain carbon number of 12 (\textit{T8, T9, T10}), there is no \textit{Colh} phase observed which might be resulting from the deficiency of flexible chains. On the other hand, elongating the carbon chain increases the temperature range of the \textit{Colh} phase (Table 2.2) up to a chain carbon number of 15, as in compound \textit{3b}; further increasing of the chain length results in decreasing the temperature range. It is expected that if we increase the length further, the \textit{Colh} phase will disappear eventually and the isotropic temperature will decrease.
Table 2.1 Phase transitions of compounds $T_{12}$, $3a$, $T_{14}$, $3b$ and $T_{16}$ at the rate of 5 °C/min from DSC on cooling.

<table>
<thead>
<tr>
<th>Compounds (length of chain)</th>
<th>Transition temperatures (°C) and enthalpy changes (Jg$^{-1}$ in [ ])</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{12}$ (12)</td>
<td>Iso 139.67 [1.15] Col$<em>{h}$ 137 [7.74] Col$</em>{ho}$</td>
</tr>
<tr>
<td>$3a$ (13)</td>
<td>Iso 138.89 [2.31] Col$<em>{h}$ 125.19 [8.74] Col$</em>{ho}$</td>
</tr>
<tr>
<td>$T_{14}$ (14)</td>
<td>Iso 135.35 [2.46] Col$<em>{h}$ 115.73 [7.26] Col$</em>{ho}$ -13.67 [10.01] Cr</td>
</tr>
<tr>
<td>$3b$ (15)</td>
<td>Iso 130.69 [2.16] Col$<em>{h}$ 104.87 [5.82] Col$</em>{ho}$ 1.98 [23.08] Cr</td>
</tr>
<tr>
<td>$T_{16}$ (16)</td>
<td>Iso 121.00 [1.9] Col$<em>{h}$ 96.7 [5.82] Col$</em>{ho}$ -9.73 [23.08] Cr</td>
</tr>
</tbody>
</table>

Fig. 2.7 Isotropic temperature vs. number of alkyl chains for compounds $T_{12}$, $3a$, $T_{14}$, $3b$ and $T_{16}$. 
Table 2.2  Temperature range of hexagonal columnar LC phase for compound T12, 3a, T14, 3b and T16.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Temperature range of Colh phase(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T12</td>
<td>2.67</td>
</tr>
<tr>
<td>3a</td>
<td>13.7</td>
</tr>
<tr>
<td>T14</td>
<td>19.62</td>
</tr>
<tr>
<td>3b</td>
<td>25.82</td>
</tr>
<tr>
<td>T16</td>
<td>24.3</td>
</tr>
</tbody>
</table>

The data of temperature ranges in Table 2.2 confirms the choice of chain lengths from 12 to 16, optimally 15, as a successful attempt at a mesogenic porphyrin with columnar phases.

2.3.2 Polarized Optical Microscopy of Compounds 3

Compound 3a is taken as an example to illustrate the thermal behavior of these porphyrin-based compounds under POM. To begin the study, the original crystal was heated until the material reached its isotropic phase. A fan texture which is characteristic to the formation of a hexagonal columnar phase was formed upon cooling from the isotropic phase. During the second heating, the texture gradually melted at the isotropic temperature, 156 °C. On the second cooling, the fan texture reappeared at 148 °C. Once the transition from isotropic phase to the columnar phase was complete, there was no significant texture change upon further cooling. Though there was an expected transition of Colh to Colho based on DSC at about 125 °C, no change in the texture was noted near this temperature. The fan texture persisted unchanged through room temperature (Fig. 2.8).
Fig. 2.8 Microscope textures of 3a on heating a) room temperature, b) 130 °C, c) 148 °C, d) isotropic at 156 °C and on cooling e) 146 °C, f) 141 °C, g) 136 °C, h) room temperature.
Typical fan textures were obtained for both porphyrin compounds 3a and 3b indicating a columnar LC phase. The phase transition from \textbf{Col}_h \text{ to } \textbf{Col}_h \text{ho} is not observable but the DSC thermogram clearly shows the existence of this transition. In summary, the porphyrin compounds 3a and 3b exhibit the following sequence on cooling from isotropic phase: \textbf{Iso} \rightarrow \textbf{Col}_h \rightarrow \textbf{Col}_h \text{ho} \rightarrow \textbf{Cr}.

\textbf{2.4 Synchrotron X-ray Diffraction of Compound 3b}

The X-ray diffraction results obtained from the thin film of 3b confirmed the homeotropic alignment of the hexagonal columnar LC phase. Typically, bulk and thin film samples are prepared to confirm a hexagonal LC phase. In this work, only the thin film samples were prepared to confirm the hexagonal phase. The phase behavior is assigned based on a combination of X-ray, DSC and POM results. A synchrotron X-ray Diffraction Study was carried out by Dr. Kumar’s group at Argonne National Laboratory.

The sample was first brought into homeotropic alignment by slowly cooling the sample from the isotropic phase to room temperature. After obtaining the homeotropic alignment, the X-ray data was then recorded upon the heating of the sample. Specific X-ray diffraction patterns and intensity vs. angle plots were taken at the temperatures of 36.7 °C, 56.7 °C, 119.1 °C and 124.3 °C. These temperatures were selected because each exhibits a different phase or phase change to be described as follows.
Fig. 2.9 X-ray diffraction patterns and intensity vs. diffraction angle plot from thin film of 3b in 8µm thick cell at 36.7 °C: a) synchrotron X-ray diffraction pattern, b) X-ray intensity vs. diffraction angle plot, c) the azimuthal scan of the peak in a).

Fig. 2.9 shows the X-ray data for the sample at 36.7 °C. The six diffraction spots in Fig. 2.9a represent the uniformly aligned hexagonal columnar phase. X-ray intensity vs. 2θ plot has a very sharp peak corresponding to 44.3 Å (calculated from 2θ using Bragg’s Law, θ is the diffraction angle), which means that the interatomic d-spacing is 44.3 Å. The azimuthal scan of the peak at 44.3 Å in Fig. 2.9c clearly demonstrates the 6-fold symmetry of the diffraction peaks with uniform intensity distribution.

With the increasing of temperature, the d-spacing increases slowly. From observations of the DSC, there is no phase change from 36.7 °C to 56.7 °C. In this temperature range, the material is in an ordered hexagonal columnar LC phase (Col\textsubscript{ho}). At 56.7 °C, the d-spacing is 44.5 Å which increased only slightly from the d-spacing at 36.7 °C.
**Fig. 2.10** X-ray diffraction pattern and intensity vs. 2θ plot from thin film of 3b in 8µm thick cell at 56.7 °C: a) synchrotron X-ray diffraction pattern, b) X-ray intensity vs. diffraction angle plot.

**Fig. 2.11** X-ray diffraction pattern and intensity vs. 2θ plot from thin film of 3b in 8µm thick cell at 119.1 °C: a) synchrotron X-ray diffraction pattern, b) X-ray intensity vs. diffraction angle plot with its expanded plot in the top right corner.
When the temperature was increased to 119.1 °C, pairs of diffraction spots appeared instead of single dots. This is attributed to the coexistence of domains with different orientation in the sampled scattering volume (Fig. 2.11). From the intensity vs. 2θ plot we can see that two peaks coexist. The d-spacing jumps from 44.9 Å to 40.4 Å and two peaks coexist in the same temperature range. The coexistence of two columnar phases with different d-spacings indicates the phase transition from $\text{Col}_{ho}$ LC phase to hexagonal columnar LC phase ($\text{Col}_{h}$) with the increasing of temperature.

At 124.3 °C, the phase has completely transitioned to the $\text{Col}_{h}$ LC phase. The d-spacing no longer has two values, favoring the one peak at 40.4 Å as shown in Fig. 2.12b. The X-ray data also looks much clearer compared to the pattern from 36.7 °C to 124.3 °C.
It appears that the mesophase of 3b transition from Colho to Colh with the changes of diffraction patterns and d-spacing. After reaching a critical transition temperature the d-spacing drops significantly. The d-spacing changes are shown vs. temperature in Fig. 2.13. The big jump at 119.1 °C indicates the transition from Colho LC phase to Colh LC phase.

To conclude, in heating sequence, the Colho phase was observed at 36.7 °C. The phase transition from Colho to Colh was observed at 119.1 °C and a completely Colh LC phase was formed completely at 124.3 °C. The X-ray data confirms the phase sequence \( \text{Iso} \rightarrow \text{Col}_h \rightarrow \text{Col}_ho \rightarrow \text{Cr} \) studied from the thermal behavior.

**Fig. 2.13** Temperature vs. d-spacing of 3b in 8µm thick cell (Blue dots represent the sample in Colho LC phase and the red dots represent the Colh LC phase.)
2.5 Achieving Homeotropic Alignment of Columnar LCs

2.5.1 Sample Preparation

Homeotropic alignment is crucial for PV applications. In order to obtain uniform homeotropic alignment, cells were used for the study. Compound 3b was selected to study the effects on the homeotropic alignment. The material was capillary filled into different types of cells at the isotropic temperature for various investigations.

2.5.2 Obtaining of the Homeotropic Alignment

The macroscopic homeotropic alignment of these two target compounds can be obtained by simply cooling a film from the isotropic phase into the mesophases with a slow cooling rate. The sample of 3b in 5 µm cell was firstly heated to isotropic temperature at 148 °C. Then it was cooled at a very slow rate of 0.2 °C/min. The texture that appeared under slow cooling was almost completely black between crossed polarizers indicating that the columns formed by strong intermolecular self-assembly are perpendicularly aligned to the film substrates, i.e. homeotropic alignment. At the temperature just below the isotropic phase, under the microscope without polarizers, a well defined hexagonal symmetry structure was observed corresponding to the black area under crossed polarizers, see Fig. 2.14. The angle between two close branches of the hexagonal structure is about 60° which reflects the structure of a hexagonal columnar phase. Moreover, the homeotropic alignment remained stable through room temperature once the transition from the isotropic phase to the hexagonal phase Colh was complete.
2.5.3 Factors to Achieve Uniform Homeotropic Alignment

When the cooling rate is as slow at 0.2 °C/min, the material can be homeotropically aligned. Large area of defects will appear when the cooling rate increases to 2 °C/min. Thus the cooling rate from the isotropic temperature is a dominant factor for the homeotropic alignment. Besides cooling rate, other factors in achieving homeotropic alignment might be cell thickness and substrate surface treatment. In order to study these effects and to get the best homeotropic alignment, we modified the cell thickness by using cells of 5 µm, 12 µm and 22 µm, and used two different surface treatments.

Two different kinds of substrate surfaces were used for comparison. One cell has no treatment on the surface with only ITO (indium tin oxide) and the other one has antiparallel alignment. No significant difference was observed in the two different cells. The result shows that modified surface substrate treatment seems to have no bearing on obtaining uniform homeotropic alignment (Fig. 2.15).
As stated, the effect of varying thin film thickness was investigated by using three different cell gaps: 5 µm, 12 µm and 22 µm. It is clear that with the increase in cell thickness, much more of the cells area shows fan defects. As a result, the thinner the cell gap the more uniform is the homeotropic alignment obtained (Fig. 2.16). So the film thickness is a bigger factor than substrate treatment for the homeotropic alignment.

To conclude, large area uniform homeotropic alignment was obtained by thermal annealing which is controlled by cooling the sample from isotropic temperature. The dominant factors to achieve homeotropic alignment appear to be cooling rate and film
thickness. The slower the cooling rate and the thinner the film, the more uniform homeotropic alignment can be achieved. The cell surface treatment has a minor effect on the formation of alignment.

2.6 Optical Properties

2.6.1 UV-vis Spectra

The absorption spectra of the porphyrins consist of a strong absorbance with the maximum at about 419 nm wavelength known as the Soret band and four weaker absorption bands known as the Q bands, which appear at 449 nm, 515 nm, 552 nm, 601 nm respectively. Taking 3b as an example, a typical UV-vis spectrum is shown below.

![UV-vis spectrum of compound 3b in methylene chloride.](image)

The molar absorption coefficients are calculated from the equation below.

\[ \varepsilon = \frac{A}{c \cdot L} \]
Where $\varepsilon$ is the molar absorptivity, $A$ is the measured absorbance, $L$ is the pathlength through the sample and $c$ is the concentration of the solution. The molar absorption coefficients of compounds 3a and 3b excited at their Soret band are listed below in Table 2.3. As we can see, molar absorption coefficients of these two compounds all exceed $10^5$ M$^{-1}$ cm$^{-1}$, which is among the highest for organic compounds.

**Table 2.3** Molar absorption coefficients of the maximum absorption wavelength for compounds 3a and 3b.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Maximum Absorption Wavelength (nm)</th>
<th>Absorption Coefficient ($10^5$ M$^{-1}$cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a</td>
<td>419</td>
<td>4.7</td>
</tr>
<tr>
<td>3b</td>
<td>418</td>
<td>5.3</td>
</tr>
</tbody>
</table>

In solution, the anisotropic porphyrin molecules are assumed to be unordered isotropic state. Considering that the ordered columnar structure may have effect on the UV-vis absorbance, thin films of different thicknesses of 3b were prepared for this investigation. To avoid the UV absorption from glass, quartz plates were used instead for the fabrication of cells. Quartz plates were ordered from United Silica Products. Product GE 124 was selected for our research study for its low absorption over a wide range; there is almost no absorption above 300 nm (Fig. 2.18).
Thin films of $3b$ were obtained in 2 µm and 4 µm thicknesses by capillary filling material $3b$ into the quartz cells followed by slowly cooling the cells at the rate of 0.2 °C/min. The results showed that the thicker 4 µm film has more intense absorption than 2 µm film. This 4 µm film successfully broadens the absorbance band in the ultraviolet region. The blue shift of the Soret band (419 nm) in solution compared with that in 2 µm film indicates the formation of untilted or less tilted stacks (H-aggregates).$^{54,55}$
The absorption of the Q band in methylene chloride is extremely low. The 4 µm thin film has a significant increase at the Q band region especially at the wavelength of 516 nm (Fig. 2.20). Basically, the thicker the film is, the higher the absorption would be.

**Fig. 2.19** UV-vis spectra of 3b in methylene chloride (dark blue line), 2µm (pink line) and 4 µm thick (turquoise line) thin films.

**Fig. 2.20** Q band of 3b in methylene chloride (dark blue line), 2µm (pink line) and 4 µm thick (turquoise line) thin films.
2.6.2 Fluorescence Spectra

Fluorescence occurs when a molecule relaxes to its ground state after being excited. The fluorescence spectra of compounds 3a and 3b were measured in methylene chloride at the excited wavelength of 419 nm and 418 nm respectively. Strong fluorescence bands at about 650 and 715 nm were observed respectively with the former band having a higher intensity (Fig. 2.21). Basically, they exhibit fluorescence emission at the wavelength range between 600 nm and 800 nm.

![Fluorescence spectra of porphyrin compounds 3a (dark blue line) and 3b (pink line) in methylene chloride excited at their Soret bands.](image)

2.7 Blends of Porphyrin with C$_{60}$ and Derivative PCBM

As mentioned before, Chlorophyll, the best photoreceptor in nature, has the basic structure of porphyrin that is a superior electron donor, whereas fullerene is an excellent electron acceptor. Thus among all the blends, porphyrin-fullerene blend is expected to be an excellent marriage. Though an adequate blend allows for charge transport, achieving
homeotropic alignment is still necessary and nontrivial. In order to achieve good charge carrier performance, blends of porphyrin with $C_{60}$ and PCBM were studied extensively.

### 2.7.1 Initial Blend Studies

As mentioned before, $C_{60}$ and PCBM differ in the addition of a chain component to the fullerene core in the case of PCBM. This change promotes better solubility in organic solvents. Though it is assumed that PCBM will afford better blends for this reason, both blends of $C_{60}$ and PCBM were prepared to determine the effect of the additives on the homeotropic alignment of the discotic porphyrin. A series of porphyrin blends with $C_{60}$ and PCBM were prepared at different ratios to study the effects.

Four samples with molar ratios of porphyrin $3b$ to $C_{60}$ and PCBM (70:1, 50:1, 30:1 and 20:1) were prepared producing eight total samples. In all cases, porphyrin $3b$ was dissolved with $C_{60}$ or PCBM in methylene chloride with the aid of an ultrasonic bath. The solvent was evaporated from the blend under reduced pressure. The resulting mixtures were then sandwiched between microscope slides.

In order to compare these samples under the same conditions, samples were each cooled at a rate of 2 °C/min from isotropic to mesophase. Even throughout one sample, different cell areas can have different texture appearance which makes comparison between samples difficult, still some tendency can be seen. The pictures in Fig. 2.22 were taken at temperatures within the range of the columnar phase and were chosen to represent the overall tendency observed by POM. The isotropic temperature for pure porphyrin $3b$ is 133 °C by POM measurement while by mixing $C_{60}$ or PCBM with the porphyrin, the isotropic temperature decreases. Adding fullerene is analogous to
increasing the impurity of the pure compound which results in a lower melting point. The isotropic temperature for each sample is summarized in Scheme 2.4.

\[
\begin{align*}
T_{iso} & \quad 135.8^\circ C \quad 134.6^\circ C \quad 133^\circ C \quad 132.9^\circ C \\
\text{(molar ratios):} & \quad \text{(Por:C}_{60}\text{=75:1)} \quad \text{(Por:C}_{60}\text{=50:1)} \quad \text{(Por:C}_{60}\text{=30:1)} \\
& \quad \text{(Por:C}_{60}\text{=20:1)} \\
& \quad 135.6^\circ C \quad 134.9^\circ C \quad 134.9^\circ C \\
\text{(Por:PCBM=70:1)} & \quad \text{(Por:PCBM=50:1)} \quad \text{(Por:PCBM=30:1)} \\
& \quad \text{(Por:PCBM=20:1)} \quad \text{(Por:PCBM=10:1)} \\
\end{align*}
\]

**Scheme 2.4** Isotropic temperatures of 3b with C\textsubscript{60} and PCBM mixtures on heating.

As we can see in Scheme 2.4, with the increasing molar ratio of C\textsubscript{60} and PCBM, the isotropic temperatures decrease constantly. Under the POM observation, by adding more and more C\textsubscript{60} or PCBM, the alignment got worsen (Fig. 2.22). Comparatively, at the same molar ratio, especially at 30:1 and 20:1, the mixtures with PCBM have better alignment than the mixtures with C\textsubscript{60}.

In conclusion, PCBM shows greater promise for use in PV cells. At same molar ratios, PCBM blends have a better tendency to align homeotropically over large areas than the C\textsubscript{60} blends. Additionally, because of the better solubility of PCBM in organic hosts, PCBM blends are more easily made and afford higher concentrations of the additive before reaching saturation. As such, only blends of porphyrin with PCBM are considered
following this study. In particular, a blend of 3b: PCBM at 30:1 (blend 1) was noted for having the highest concentration of additive with homeotropic alignment. For this reason, \textbf{blend 1} is chosen as an example for further investigation.
Fig. 2.22 Microscope textures under crossed polarizers of 3b mixed with C₆₀ at the molar ratio of a) 70:1, c) 50:1, e) 30:1, d) 20:1 and with PCBM b) 70:1, d) 50:1, f) 30:1, h) 20:1.
2.7.2 Thermal Behavior of Blend 1

In comparison of blend 1 to the pure material 3b, it is obvious from the DSC thermogram (Fig. 2.23) that by adding PCBM, the phase transition temperatures of blend 1 decrease. The transition temperatures and enthalpies of 3b and blend 1 are summarized in Table 2.4.

![DSC thermogram of 3b (dark blue line) and blend 1 (pink line) at the cooling rate of 5 °C/min.](image)

Table 2.4 Phase transitions for porphyrin 3b and blend 1 from DSC cooling at the rate of 5 °C/min.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Transition temperatures (°C) and enthalpy changes (Jg⁻¹ in [ ])</th>
</tr>
</thead>
<tbody>
<tr>
<td>3b</td>
<td>Iso 130.69 [2.159] Colₜ 104.87 [5.817] Col₝ 1.98 [23.08] Cr</td>
</tr>
<tr>
<td>blend 1</td>
<td>Iso 123.35 [1.42] Colₜ 97.65 [3.83] Col₝ 1.9 [11.58] Cr</td>
</tr>
</tbody>
</table>

For blend 1, on cooling at a rate of 2 °C/min, it first goes into a shearable liquid crystalline phase at 131.5 °C from POM with the growth of distinct fan. The hexagonal columnar phase remains unchanged through room temperature. Homeotropic alignment
was achieved in 2 μm and 4 μm cells to a significant degree but was barely achieved in a 22 μm cell (Fig. 2.24). The Colh phase is well maintained with the addition of PCBM for blend 1. To the best of our knowledge, this was the first homeotropically aligned crystalline thin film composed of liquid crystalline porphyrin and a fullerene supramolecular complex.

![Microscope textures under crossed polarizers of blend 1 at room temperature with different thicknesses: a) 4.5, b) 12 and c) 22 μm.](image)

**Fig. 2.24** Microscope textures under crossed polarizers of blend 1 at room temperature with different thicknesses: a) 4.5, b) 12 and c) 22 μm.

### 2.7.5 Synchrotron X-ray Diffraction Study of Blend 1

The X-ray samples studied were thin films of blend 1 prepared in the same manner as for 3b in previous section. There is no significant difference observed between pure 3b and blend 1 which might due to the small amount of PCBM added. As shown in Fig. 2.25, at the temperature of 48 ºC, clear six dots representing a hexagonal phase were observed with a d-spacing of 44.7 Å. Similar phenomena was observed when the sample was heated to higher temperatures. At 121.0 ºC, the d-spacing jumped to 40.3 Å indicating the phase transition from Colh to Colh LC phase as before (Fig. 2.26). Thus blend 1 exhibits the same phase sequence as 3b of Iso→Colh→Colh→Cr.
Fig. 2.25 X-ray diffraction patterns and intensity vs. diffraction angle plot from thin film of blend 1 in 8 µm thick cell at 48 °C: a) synchrotron X-ray diffraction pattern, b) X-ray intensity vs. diffraction angle plot, c) the azimuthal scan of the peak in a).

Fig. 2.26 X-ray diffraction patterns and intensity vs. diffraction angle plot from thin film of blend 1 in 8 µm thick cell at 121 °C: a) synchrotron X-ray diffraction pattern, b) X-ray intensity vs. diffraction angle plot, c) the azimuthal scan of the peak in a).
2.7.3 UV-vis Spectra of Blend 1

The UV-vis spectra measurements were taken in a methylene chloride solution. Both 3b and blend 1 samples were controlled at the same concentration of 3b (4.64\times10^{-6} \text{ M}) for comparison. Due to the small amount of PCBM added in, there is no big effect on the UV spectra in blend 1 (Fig. 2.27). Both 3b and blend 1 exhibit a Soret band at 419 nm which is typical for porphyrin compounds.

![UV-vis spectra of mixture of 3b (dark blue line) and blend 1 (pink line) in methylene chloride.](image)

To observe changes based on the addition of PCBM, higher molar concentration solutions of PCBM were prepared. The absorption spectra of porphyrin 3b and PCBM mixture in methylene chloride changed upon the addition of PCBM. The intensity of Soret band decreased gradually when the PCBM concentration was raised, while the absorbance below 398 nm increased. The two bands that increased dramatically at around 260 nm and 367 nm are expected to be the absorption of PCBM (Fig. 2.28).
Fig. 2.28 UV-vis spectra of 3b upon the addition of PCBM at a concentration of 1.70 μM with PCBM/3b in molar ratio, 0 (plum line), 0.9 (green line), 2.1 (pink line) and 3.7 (black line).

The UV-vis spectra of blend 1 thin films in quartz cells show a behavior similar with the pure 3b compound. The thickest thin film (7 μm) has the highest absorption in almost all the region. The thicker film (4 μm) has more intense absorption than the 2 μm thin film in most regions except the region around the Soret band (Fig. 2.29). This might be attributed to the thicker film with less uniform homeotropic alignment. The Q band was red shifted and increased significantly compared to the peaks in methylene chloride.
2.7.4 Fluorescence Spectra of Blend 1

The fluorescence emission spectra of porphyrin 3b upon the addition of PCBM show that the emission of porphyrin 3b was quenched gradually by the increased addition of PCBM. This is due to an efficient electron transfer from porphyrin to PCBM in the blend system. There are two emission peaks around 665 nm and 720 nm. With the increasing of PCBM, both emission peaks went down. The peak at 665 nm decreased faster than 720 nm. It's clear that under the irradiation of 365 nm UV light, the emitted light of samples in solution becomes less and less intense with the addition of PCBM in correspondence with the fluorescence spectra (Fig. 2.30).
Fig. 2.30 Fluorescence spectra of 3b upon the addition of PCBM at a concentration of 43.7 µM and excited wavelength of 520 nm in chlorobenzene with PCBM/3b in weight ratio, 0 (blue line), 0.5 (pink line), 1 (yellow line) and 2 (bright green line). The inset shows emission image under 365 nm UV irradiation with samples from left to right corresponding to the samples from blue line to bright green line in the spectra.

2.7.5 The Packing Model of Porphyrin and PCBM

It is interesting to consider how the fullerene and porphyrin might arrange in the blend. Using estimated molecular lengths and X-ray d-spacing measurement, some hypothetical arrangements can be assumed. The diameter of porphyrin is approximately 6.5 nm, whereas the distance between the two neighboring columns (d-spacing) from XRD experiment is about 4.4 nm. So we can deduce that the interdigitation of the long flexible chains exists and that the lipid chain intercalating length $a$ is about 1.6 nm (Fig. 2.31). Considering the size of PCBM (about 0.7 nm) and its lipophilicity, one possible molecular arrangement is the hexagonal columnar phase of porphyrin with PCBM at interstices of the columns (bottom in Fig. 2.32 left). However, a more possible molecular arrangement is that PCBM is sandwiched between two porphyrin cores due to the strong
π-donor and π-acceptor interaction (top in Fig. 2.32 left). Regardless of packing arrangement, the porphyrin and PCBM supramolecular complex retains a homeotropically aligned architecture (Fig. 2.32 right) which is very important for PV applications because this favorable molecular arrangement can provide an efficient path for electrons or/and holes along the columnar axis, and the light-harvesting molecules are arranged with the largest area toward the coming light.

**Fig. 2.31** Calculated geometric dimensions of porphyrin 3b (left) and 3D ChemDraw spacing-filling model of fullerene derivative PCBM (right).
2.8 The Bilayer Heterojunction and Bulk-heterojunction Solar Cells

Using Porphyrins as Donors

2.8.1 Cell Fabrication and Characterization

The cell fabrication and characterization were carried out by Dr. Dai’s group in University of Dayton. The heterojunction solar cell consisted of a bilayer film of porphyrin and C_{60} sandwiched between a transparent anode (ITO glass) and a metal cathode (Al/Ca). The bilayer film was replaced by a single layer thin film of the porphyrin and PCBM blend in the bulk-heterojunction device. A 30 nm thick poly(3,4-ethylenedioxythiphene): poly(styrenesulfonate) (PEDOT:PSS) layer was deposited by spin coating from an aqueous solution onto the ITO coated glass substrates, followed by baking at 150 °C for 15 minutes. For the heterojunction devices, the bilayer photoactive film (30 nm C_{60}/ 80 nm porphyrin) was prepared by first spin coating a porphyrin solution in chlorobenzene on top of the PEDOT/ITO anode, and then by thermally...
depositing C\textsubscript{60} under vacuum of \textasciitilde10\textsuperscript{-6} Torr. In the case of bulk-heterojunction devices, a porphyrin and PCBM (1:1 w/w) solution in chlorobenzene was spin coated on top of the PEDOT/ITO anode to form the photoactive layer of \textasciitilde 230-250 nm in thickness. Thereafter, a 15 nm thick Ca and 150 nm thick Al films were successively deposited thermally onto the photoactive layer through a physical mask under vacuum of \textasciitilde10\textsuperscript{-6} Torr to act as the cathode in both the bilayer heterojunction and bulk heterojunction devices (Fig. 2.33). The post annealing was carried out by heating the device on a hot stage from room temperature to \textasciitilde140 °C and held for about 10 minutes, followed by subsequently cooling down from 140 °C to 80 °C with an average cooling rate of 0.2 °C/min and from 80 °C to room temperature with a cooling rate of 5 °C/min. The current-voltage (I-V) curves were recorded on a Keithly 236 source measurement unit, while the photocurrent was measured under simulated AM 1.5G irradiation (100 mW/cm\textsuperscript{2}) using a xenon lamp based solar simulator (XPS-400, Solar Light Co.).

Fig. 2.33 Schematic representations of the bilayer heterojunction and bulk-heterojunction solar cells.
2.8.2 Results and Discussion

Compared to the bilayer heterojunction devices, the bulk heterojunction solar cells showed much improved device performance which might be attributed to the limited interfacial area between the donor and acceptor layers as the electron-hole separation only occurred at the donor-acceptor interface in bilayer heterojunction devices. Post annealing was shown to improve the device performance significantly for both the layered and bulk heterojunction solar cells due to the homeotropic alignment of porphyrins in the photoactive layers. After annealing, the bulk heterojunction devices exhibited power conversion efficiencies (PCEs) of 0.528% and short circuit current density \(J_{sc}\) of 3.720 mA/cm\(^2\) and prior to annealing, the PCEs and \(J_{sc}\) were 0.081% and 0.740 mA/cm\(^2\) respectively.

It is noticed that postannealing indeed induced a more than 500% increase in both \(J_{sc}\) and PCE presumably due to the thermally induced alignment of porphyrin layer. This confirms that the homeotropic aligned porphyrin could provide a more efficient pathway for hole conduction along the columnar axis than the unaligned sample.\(^5\)

2.9 Conclusion

Two target liquid crystalline porphyrins 3a and 3b were synthesized. Their chemical structures were well identified by \(^1\)H NMR, \(^{13}\)C NMR, IR, Mass Spectrometry and Elemental Analysis. Their thermal behavior was fully studied by POM and DSC. Typical fan textures of a columnar LC phase were observed. Transition temperatures and enthalpies were recorded by DSC thermogram. The mesophases of 3 were confirmed by Synchrodron X-ray diffraction. These materials have the phase sequence:
Iso→Colₜ→Colₜₒ→Cr. As discussed above, the homeotropic alignment is a key issue for the PV application. Compounds 3 can homeotropically aligned without external stimuli such as alignment coating or polarized infrared light and remained unchanged through room temperature. The factors in obtaining the homeotropic alignment were investigated. The results show that cooling rates and uniform cell thickness are important for obtaining uniform homeotropic alignment.

Both compounds in solvent and sandwiched between cells of different thicknesses were studied under UV-vis spectra. Porphyrins 3 have strong absorption at the Soret band and strong emission at the excited wavelength which is highly fluorescent.

The bilayer-heterojunction and bulk-heterojunction solar cells using mixture of 3b with C₆₀ and PCBM were fabricated by Dr. Dai’s group in Dayton. The results show that the bulk-heterojunction solar cells have better performance than the bilayer-heterojunction cells and with the treatment of annealing, the PCEs is 0.528%. Since to a full homeotropic alignment may be difficult in the blend system with PCBM with the weight ratio of 1:1, we can expect a promising performance with much higher efficiency by improving the alignment.

Homeotropic alignment for the first time was achieved for the porphyrin-PCBM blend which can provide an efficient pathway for the electron-hole conduction. The mixture of blend 1 shows similar phase behavior and optical properties with pure compound 3. The optical measurements show a strong absorption at the solar energy band. Upon the addition of PCBM, the intensity of Soret band in UV-vis spectra was decreased and the fluorescence emission was quenched gradually which indicates successful electron
transfer from porphyrin donor to PCBM acceptor. So this porphyrin-fullerene blend material would be feasible for solar cells.
Chapter 3

Fluorinated Porphyrins

Part of this chapter is also available in


3.1 Molecular Design of Fluorinated Porphyrins

Homeotropic alignment was obtained by controlling the cooling rate and cell thickness for target porphyrins made in Chapter 2. However, the alignment highly depends on the cooling rate which does not favor device fabrication. In order to make the homeotropic alignment easier to achieve, we modified the side chains of the porphyrin in this Chapter.

3.1.1 Some Previously Reported Fluorinated LCs

Perfluoroalkyl compounds have been shown to increase molecular rigidity and cause a fluorophobic interaction. Because of these special features, many commercial LCs and research are made by replacing some or all of the hydrogens on a molecule with fluorine
atoms. This change improves the thermal stability of their calamitic LC phase. For example, in 1991, Takashi Doi et al. reported that in LC molecules (Fig. 3.1)\textsuperscript{57}, the fluoroalkyl group can increase the smectic properties and enhance the $S_A$-$I$ transition temperature. They also observed the monolayer or the interdigitated arrangement in the smectic phases of these perfluoroalkyl compounds.

![Chemical structures of liquid crystals with different perfluoroalkyl chains](image)

Fig. 3.1 Chemical structures of liquid crystals with different perfluoroalkyl chains ($R_1 = C_nH_{2n+1}$ ($n = 1$-$8$), $R_2 = CH_2(CF_2)_mF$ or $C_2H_4(CF_2)_mF$ ($m = 1$-$10$)).

A year later, Shunsuke Takenaka introduced the perfluroalkyl chain to substitute benzene (Fig. 3.2a) and found that the long perfluoroalkyl group is indispensable for the realization of a smectic phase.\textsuperscript{58} Moreover, Cumming et al. explored detailed studies on the effect of a perfluoroalkyl chain on the phase behavior of some Schiff base LCs (Fig. 3.2b) and found that increasing the rigidity of the tail moiety of a liquid crystalline compound will enhance the stability of the smectic A phase and destabilize the smectic C phase at the same time.\textsuperscript{59}
Fig. 3.2 Chemical structure of a) liquid crystals having a single benzene ring with perfluoroalkyl chain, b) Schiff base liquid crystals with a perfluoroalkyl chain.

However, if a molecule becomes more and more rigid, the LC properties diminish; so it’s reasonable to combine both less rigid hydrocarbon chains and perfluoroalkyl chains within the same molecule. Wilson’s group has applied this kind of chain on the backbone of the different polymer: polyesters \([-\text{OCH}_2\text{CH}_2\text{N(SO}_2\text{CF}_2)_8\text{F}\text{CH}_2\text{CH}_2\text{O}_2\text{CR}_m\text{CO}]_n\) with \(m=2-10\) inclusive and \(m=12, 20\) and fluorocarbon-hydrocarbon microblock(-
and found that both polymers have either a smectic A or smectic B phase. The mesophase transition temperatures and enthalpies are also found to vary with the change of hydrocarbon content. From X-ray, the difference in spacing was observed to increase as the hydrocarbon increases. Later on, the same group also implemented this kind of semifluorinated chain on the side chain of a polymer. Similar to previous results, this kind of chain led molecules to form a highly ordered lamellar thermotropic mesophase due to microsegregation. Kuwahara et al. also found that this kind of microsegregation could lead to a lyotropic mesophase. This brought about a more specific question relevant to this work: what if this kind of semifluorinated hydrocarbon chain is introduced into the discotic LC molecules? Actually, researchers have already discovered that a dramatic stabilization of the hexagonal columnar mesophase is generated from supramolecular and macromolecular columns with semifluorinated alkyl chains. For example, Johansson et al. reported that with the help from the semifluorinated hydrocarbon chain, even a single substituted benzene unit could exhibit classic smectic phases (Fig. 3.3). More specifically, Shimizu’s group attached this kind of semifluorinated hydrocarbon to the peripheral chain of triphenylene mesogens and found a strong tendency towards homeotropic alignment of the hexagonal columnar (Colh) mesophase. The authors conclude “the introduction of perfluoromethylene chains into the peripheral tails of discotic liquid crystals may provide molecular design technique for realizing a spontaneous homeotropic alignment of a Colh phase.”
3.1.2 Design of Target Fluorinated Porphyrins

As mentioned above, perfluorinated alkyl chains have a special property in stabilizing the LC phase especially for discotic LCs and fluorine substitutions at the alkyl carbon atoms have some advantages since they are more rigid. Thus, we modified the porphyrin target structure by introducing partially perfluoroalkyl chains as the terminal side chains. To our delight, with this change, we’ve achieved homeotropic alignment of almost the entire cell area and within large temperature regimes.

3.2 Preparation of Fluorinated Porphyrins

The porphyrin with partially perfluorinated compounds were synthesized generally from perfluorohexyl iodide by radical addition, reduction, bromination, Williamson ether formation, hydrolysis and ester formation in six steps.

3.2.1 Synthesis of the Iodo Substituted Partially Perfluorinated Alkyl Alcohol
The synthesis was started from the fluorinated iodide and allylic alcohols. The copper-catalyzed addition of perfluorohexyl iodide to allylic alcohols 4a-4c was carried out in a sealed tube and heated to 120 °C for about 3 hours in high yield.

When 11,11,12,12,13,13,13-heptafluoro-10-iodo-tridecan-1-ol 4d was synthesized using the same procedure as above, the yield was pretty low. It was noted that the boiling point of perfluorohexyl iodide is 117 °C and the boiling point of heptafluoro-1-iodopropane is only 41 °C. And this copper catalyzed radical addition needs temperature as high as 120 °C. So it is assumed that the heptafluoro-1-iodopropane evaporated very quickly leading to an uncompleted reaction with lots of the unsaturated alcohols. This step was changed to a palladium (0)-catalyzed radical addition, which can be held just at room temperature. 11,11,12,12,13,13,14,14,14-nonafluoro-10-iodo-tetradecan-1-ol 4c was also synthesized via (Ph₃P)₄Pd(0) catalyzed addition.

\[
\begin{align*}
\text{IR} &+ \text{OH} \\
\text{Cu} &\rightarrow \\
\text{IR} &+ \text{OH} \\
\end{align*}
\]

Scheme 3.1 Synthetic scheme of the iodo substituted partially perfluorinated alkyl alcohol 4.
3.2.2 Synthesis of Partially Perfluorinated Alkyl Alcohol

The alcohol derivatives were prepared by lithium aluminum hydride reduction. The reaction was refluxed under air free conditions for 4 hours. After the reaction was complete, a small amount of H₂O was added slowly into the mixture at 0 °C to destroy the pyrophoric lithium aluminum hydride residue. The small amount of crude compounds obtained, which, based on the reaction mixture’s appearance could be due to the aluminum hydroxide residue surrounding the product, preventing it from dissolving in organic solvent. To solve this problem we added diethyl ether to the mixture after filtration and refluxed again to recover more products.

\[
\begin{align*}
\text{R} & \quad \text{LiAlH}_4 \quad \text{Et}_2\text{O} \\
\text{R} & \quad \text{R} \quad \text{LiAlH}_4 \quad \text{Et}_2\text{O}
\end{align*}
\]

\[5a. \quad \text{R}=\text{C}_6\text{F}_{13} \quad n=2 \]
\[5b. \quad \text{R}=\text{C}_6\text{F}_{13} \quad n=8 \]
\[5c. \quad \text{R}=\text{C}_8\text{F}_{17} \quad n=2 \]
\[5d. \quad \text{R}=\text{C}_3\text{F}_7 \quad n=8 \]
\[5e. \quad \text{R}=\text{C}_4\text{F}_9 \quad n=8 \]

**Scheme 3.2** Synthetic scheme of partially perfluorinated alkyl alcohol 5.

3.2.3 Synthesis of Partially Perfluorinated Alkyl Bromide

The bromination step was carried out in aqueous 48% HBr with the phase transfer reagent cetyltrimethylammonium bromide. The reaction mixture was refluxed for 8 hours. After the reaction completed, the mixture was extracted and went to the next step without further purification.
Scheme 3.3 Synthetic scheme of partially perfluorinated bromide 6.

3.2.4 Synthesis of Benzoates and Benzoic Acids with Partially Perfluorinated Alkyl Chains

The benzoate compounds 7 were prepared by the Williamson ether formation. Then benzoic acids 8 were synthesized via the hydrolysis process using the same procedure as in Chapter 2.

Compounds 7 were purified by flash chromatography and identified by NMR spectra. Taking 7d as an example, NMR spectra of the product shows a nice one singlet peak at 7.26 ppm in aromatic region, suggesting that there is only one aromatic compound in the product. In the chemical shift 3-5 ppm region, there is a singlet peak at 3.89 ppm, which is the ArCOOCH$_3$ peak; there is a multiple peak at around 4.02 ppm, which has integration ratio of 3:1 compared with the aromatic proton, suggesting that three alkylation happened in all the phenol groups (Fig. 3.4). This is also confirmed with the carbon spectrum at 73.12 ppm, the ether carbon in the middle of the three alkyl chain; 69.11 ppm, the two ether carbons in the side of the three alkyl chain and 52.11 ppm, carbon of the methyl ester (Fig. 3.5). Above all, NMR spectra firstly suggests that our desired product exists without other aromatic impurity. Now regarding to aliphatic
impurities, since in the previous step the alkene reactant is excess, after the alkylation step the possible aliphatic we got should be the 4-butene-1-ol derivatives. In the work-up condition of these two steps (evaporate under vacuum etc.), low boiling point impurities were removed. In our case, if there are impurities, it’s likely this impurity will have alcohol present. This leads to the fact that if there are impurities, we should see the two protons near this alcohol group in the region. However there is no such proton peak, so NMR spectra show that we have a pure desired product.

\[
\text{Scheme 3.4 Synthetic schemes for the preparation of benzoates 7 and benzoic acids 8 with partially perfluorinated chains.}
\]
Fig. 3.4 Proton NMR spectrum of compound 7d.
3.2.5 Synthesis of Target Fluorinated Porphyrins

The target compounds 9 were synthesized by ester formation reaction. Unfortunately only 9a, 9d and 9e could react with the porphyrin core. The reason could be that the long fluorinated side chains reduce the solubility of the acids dramatically in organic solvent for the reaction hard to proceed.
**Scheme 3.5** Synthetic scheme of target fluorinated porphyrins 9.

9a. \( R = C_6F_{13} \quad n = 4 \)
9d. \( R = C_3F_7 \quad n = 10 \)
9e. \( R = C_4F_9 \quad n = 10 \)
3.3 Thermal Behavior

The thermal behavior of the target porphyrins are identified by DSC and POM. The phase transitions from DSC are summarized in Table 3.1. From 9d and 9e, it can be seen that increasing the fluoro length causes the isotropic temperature to increase, which is an opposite trend from the nonfluorinated porphyrins. For 9a with six perfluoro chains, there is an exothermic peak at 398 °C on first heating which means it could have decomposed at this point before reaching the isotropic temperature. The DSC thermograms are shown in Fig. 3.6.

Table 3.1 Phase transition and transition enthalpy changes of 9a, 9d and 9e at the rate of 5 °C/min from DSC on cooling.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Transition temperatures (°C) and enthalpy changes (Jg⁻¹ in [ ] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>9a</td>
<td>P 198.83 [3.709] Cr</td>
</tr>
<tr>
<td>9d</td>
<td>Iso 221.64 [1.228] Colh 123.45 [2.017] Colho/Cr</td>
</tr>
<tr>
<td>9e</td>
<td>Iso 240.45 [2.724] Colh 120.18 [4.107] Colho/Cr</td>
</tr>
</tbody>
</table>
Taking 9e as an example, the Colh phase range is between 240 °C and 120 °C on cooling and has been observed similarly by optical microscopy. Upon further cooling from 120 °C, the phase is assumed to become a more ordered hexagonal columnar LC phase (Colho) or hexagonal crystalline phase in coordination with the nonfluorinated
analogue. The exact phase structure is yet to be confirmed. Unlike the nonfluorinated porphyrins, it is noted that the thermal ranges of the hexagonal columnar liquid crystalline phases are wider by more than 100 °C.

For microscope observations, samples were prepared by capillary filling porphyrins into 5 µm barely ITO coated cells at their isotropic temperature. The phase sequences were observed for 9e by cooling the samples from the isotropic temperature of 250 °C with the cooling rate of 2 °C/min. During the cooling process, very few birefringent defects or fan textures appeared under POM (Fig. 3.7a). An almost entirely black area between crossed polarizers was obtained indicating an exceptionally strong tendency towards homeotropic alignment. Similar to the nonfluorinated porphyrins, under the microscope without polarizers, hexagonal symmetry patterns appeared just below the isotropic temperature indicating the hexagonal columnar phase (Fig. 3.7b).

In summary, by combining DSC and POM results, the porphyrin compounds 9d and 9e exhibit the phase sequence \( \text{Iso} \rightarrow \text{Col}_h \rightarrow \text{Col}_{ho}/\text{Cr} \) on cooling from the isotropic phase.

Fig. 3.7 Microscope textures of 9e at 237.7 °C on cooling a) under crossed polarizers, b) without polarizers.
3.4 Synchrotron X-ray Diffraction Study of Compound 9e

To confirm the phase sequence studied by DSC and POM in the previous section, synchrotron X-ray diffraction study were carried out by Dr. Kumar’s group. Thin films and bulk samples of 9e were prepared for X-ray diffraction study. The thin film sample was sandwiched by 50 µm thick bare glass plates with 8 µm thickness and the bulk sample was sandwiched by Kapton films which is an unaligned powder film. The X-ray data was recorded upon slow cooling of the samples from the isotropic phase to the mesophase for both the glass cell and the bulk sample.

Fig. 3.8 Powder X-ray diffraction patterns of 9e at 243 °C a) large angle scattering, b) small angle scattering.

The diffraction pattern from isotropic temperature in Fig. 3.8a shows that it consists of two diffuse rings at a large angle (outside ring) and a small angle (inner ring) scattering corresponding to the d-spacing of 5.5 Å and 39.0 Å respectively. Fig. 3.8b is the
expansion of the inner small angle ring from Fig. 3.8a. These rings are typical for the isotropic phase. Upon further cooling, at a temperature of 176.5 °C, the inner ring turned into three condensed rings, corresponding to three d-spacings of 41.04 Å, 23.8 Å and 20.6 Å (ratio=1: 1/√3:1/2) indicating hexagonal packing. The broad peak from the outer ring in Fig. 3.9c indicates liquid-like intracolumn positional order. Combining this diffused shape with the ordered hexagonal phase indicated by the inner ring, the hexagonal columnar LC phase can be confirmed.

![Fig. 3.9](image)

**Fig. 3.9** Powder X-ray diffraction patterns of 9e at 176.5 °C a) large angle scattering, b) small angle scattering, c) intensity vs. diffraction angle plot.

The d-spacing increases upon decreasing the temperature within the same mesophase. When the temperature reached 151 °C, the d-spacing had increased to 41.56 Å, 24.06 Å and 20.84 Å (Fig. 3.10). At 122.7 °C, the d-spacing was measured as 42.3 Å, 24.5 Å and 21.2 Å (Fig. 3.11) which still retained the hexagonal ratio of 1: 1/√3:1/2.
Fig. 3.10 Powder X-ray diffraction patterns of 9e at 151 °C a) large angle scattering, b) small angle scattering, c) intensity vs. diffraction angle plot.

Fig. 3.11 Powder X-ray diffraction patterns of 9e at 122.7 °C a) large angle scattering, b) small angle scattering, c) intensity vs. diffraction angle plot.

The thin film X-ray patterns at 176 °C and 151 °C are shown in Fig. 3.12. At the high temperature of 176 °C (Fig. 3.12a), the scattering intensity is so low that we can only observe six spots at the d-spacing of 40.4 Å. With a lower temperature at 151 °C (Fig. 3.12b), three d-spacings (40.4 Å, ~ 23.3 Å and ~ 20.2 Å) at different angles appeared demonstrating the hexagonal structure.
Fig. 3.12 Thin film X-ray diffraction pattern of 9e at a) 176 °C and b) 151 °C.

Upon further cooling to 126 °C, the three circles of six diffraction dots became much more clear and intense. This pattern in Fig. 3.13a is similar to crystal diffraction. This phenomenon, to our best knowledge, hasn’t been found in the hexagonal LC phase, and clearly demonstrates the hexagonally packed columnar phase. The d-spacings are 41.5 Å, 24.0 Å, and 20.8 Å (Ratio = 1: 1/√3:1/2). The azimuthal scans of the each peak (Fig. 3.13c, d and e) confirm the hexagonal columnar phase with a homeotropic orientation.
Fig. 3.13 Thin film X-ray diffraction data of 9e at 126 °C a) synchrotron X-ray diffraction pattern, b) X-ray intensity vs. diffraction angle plot, c) the azimuthal scan of the peak in a at d=41.5 Å, d) the azimuthal scan of the peak in a at d=24 Å, e) the azimuthal scan of the peak in a at d=20.8 Å.

At the temperature of 82.9 °C which is below the Colh phase, the main peak at d=−44 Å was blocked by the beam stop so only the outer two circles of hexagonal diffraction dots at 25.7 Å and 22.3 Å can be observed (Fig. 3.14). Thus, the azimuthal peak scan of d=44 Å is unresolved (Fig. 3.14b). The azimuthal scan at the peak of 25.7 Å (Fig. 3.14c) verifies the hexagonal order of columns. Powder X-ray diffraction pattern at 102.9 °C confirms the hexagonally ordered columnar structure but it remains unclear whether it’s a
LC phase or a crystalline phase (Fig. 3.15). Furthermore, since the transition peak from Col\textsubscript{ho} to the crystalline phase was not observed until -30 °C by DSC, this phase could be a hexagonal ordered crystalline phase.

**Fig. 3.14** Thin film X-ray diffraction data of 9e at 82.9 °C a) synchrotron X-ray diffraction pattern, b) the azimuthal scan of the peak in a at d=44 Å, c) the azimuthal scan of the peak in a at d=25.7 Å.

**Fig. 3.15** Powder X-ray diffraction patterns of 9e at 102.9 °C a) large angle scattering, b) small angle scattering, c) intensity vs. diffraction angle plot.
In conclusion, the phase sequence was identified by small angle scattering of thin film and large angle scattering with bulk sample. By combining the X-ray results with DSC and POM, we can confirm the hexagonal columnar LC phase exists at the temperature range from 120 °C to isotropic temperature 240 °C. At the temperature below 120 °C, the phase could be either Col_{ho} or crystalline phase.

### 3.5 Homeotropic Alignment of Compound 9e

Previously, in order to obtain a high degree of homeotropically aligned nonfluorinated porphyrin, the cooling rate could be no faster than 0.2 °C/min. In contrast, the fluorinated porphyrin 9e shows a similar tendency towards complete homeotropic alignment with cooling rates even as fast as 10 °C/min. Based on this improvement, it can be stated that the fluorinated porphyrins are much easier to be aligned than the nonfluorinated compounds. In addition to cooling rate, cell thickness and surface treatment are also looked at as before.

When cooling 9e at a rate of 10 °C/min from the isotropic temperature, most of the cell area remains black between crossed polarizers indicating homeotropic alignment. When cooled to room temperature, the black homeotropic areas became speckled with grey, but were still comparably black (Fig. 3.16a). To confirm homeotropic alignment at room temperature, a conoscope image was taken. As seen in Fig. 3.16c, a clear cross at the center characteristic of the homeotropic alignment was observed.
The alignment dependence on different thickness of fluorinated samples was investigated by varying the cell thickness. Cells with 5 µm, 9 µm and 20 µm thickness were used for this study. All the cells are spin coated with polyimide rubbed and assembled with antiparallel alignment. Compound 9e and its nonfluorinated counterpart T14 with the same alkyl length were selected for comparison (Fig. 3.17).
Fig. 3.17 Microscope textures under crossed polarizers of 9e and T14 in 5 µm, 9 µm and 20 µm thickness cells at room temperature.

The results showed that for 9e, almost complete homeotropic alignment was achieved for both 5 µm and 9 µm cells, while a few and large areas of defects were observed for T14 in 5 µm and 9 µm cells respectively. In the much thicker 20 µm cell, many defects were observed for both materials (Fig. 3.17). From the observation above, 9e has stronger
tendency to be homeotropically aligned than T14. And the cell thickness remains a factor for the alignment with a preference towards thinner cells.

To study the surface treatment effect on the alignment, compound 9e in two 9 µm cells with different surface substrates were studied under POM. One cell’s substrate was antiparallel polyimide and the other cell’s substrate was bare ITO glass. Both samples were cooled at the same rate of 2 °C/min. As shown in Fig. 3.18, both samples obtained homeotropic alignment easily, indicating that the substrate treatment is not a key issue for the homeotropic alignment of this material.

**Fig. 3.18** Homeotropically aligned microscope textures of 9e in 9 µm antiparallel cell a) under crossed polarizers, b) without polarizers and in 9 µm bare ITO cell, c) under crossed polarizers, d) without polarizers.
3.6 Sheared Texture of Porphyrin 9e

Besides the homeotropic alignment, uniform homogeneous alignment can be easily achieved by mechanical shearing from a homeotropically aligned state. The sample was prepared by sandwiching 9e between microscope slides. The material was firstly heated to isotropic phase and then cooled at the rate of 2 °C/min to obtain the homeotropic alignment. At 220 °C, which is just below the isotropic temperature, the sample was sheared toward one direction mechanically. Thus, a uniform homogeneous alignment along the shearing direction was obtained. Under 45° crossed polarized light, we can observe the homogeneous alignment clearer. The AFM image observed from the thin film of the sample 9e on glass substrate is also a confirmation for this alignment (Fig. 3.20). Simple schematic representation of this process is shown below in Fig. 3.19.
Fig. 3.19 Homogeneously aligned microscope texture of 9e achieved by mechanically shearing a homeotropically aligned cell at 220 °C a) homeotropically aligned texture before shearing at 220 °C under crossed polarizers, b) homeotropically aligned texture before shearing without polarizers, c) homogeneous aligned texture after shearing under crossed polarizers (arrow indicates shearing direction), d) homogeneous aligned texture under 45° polarizers, e) schematic representations of homeotropic alignment to homogeneous alignment after shearing.

Fig. 3.20 AFM image of 9e on glass substrate.
3.7 Optical Properties

3.7.1 UV-vis Spectra

The absorption spectra of the fluorinated porphyrins are similar to the nonfluorinated compounds. The molar absorption coefficients of the maximum absorption wavelength for compounds 9 are summarized in Table 3.2. Compound 9e is taken as an example to illustrate the optical properties of the fluorinated porphyrins. Like the nonfluorinated porphyrins, the highest absorbance peak was obtained at 419 nm. The thin film of 9e in 2 µm cell was also investigated to observe the alignment effect on UV-vis absorption. Compared to the material in organic solvent without any order, compound 9e in a 2 µm cell has ordered homeotropic alignment which leads to the blue shift of the Soret band from 419 nm to 408 nm. Again, a blend with PCBM was made by adding PCBM in molar ratio of 1:1, a blue shift from the peak in solution at the Soret band in the 2 µm cell was observed (Fig. 3.21).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Maximum Absorption Wavelength (nm)</th>
<th>Absorption Coefficient ($10^5$ M$^{-1}$cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9d</td>
<td>419</td>
<td>4.8</td>
</tr>
<tr>
<td>9e</td>
<td>419</td>
<td>5.2</td>
</tr>
</tbody>
</table>
**Fig. 3.21** UV-vis spectra of 9e in methylene chloride (dark blue line, c=3.7 µM), 2 µm cell (pink line) and its blend with PCBM (bright green line, molar ratio=1:1) in 2 µm cell.

### 3.7.2 Fluorescence Spectra

Similar with other porphyrins targets, the fluorescence spectrum of 9e in chlorobenzene has two emission bands at 658 nm and 716 nm. By adding PCBM, the intensity of emission spectra decreased due to intramolecular electron transfer. When adding a small amount of PCBM in molar ratio 1:1 (9e: PCBM) the quenching effect is small while by adding PCBM in weight ratio 1:1 (9e: PCBM), the intensity was significantly decreased as expected (Fig. 3.22).
3.8 Conclusion

Three fluorinated porphyrins of target 9 were successfully synthesized, two of which have shown a columnar LC phase. Their chemical structures were well identified by $^1$H NMR, $^{13}$C NMR, IR, Mass and Elemental Analysis. The mesophase behavior of compounds 9 was identified by DSC and POM. Compound 9e was also characterized by synchrotron X-ray diffraction. These two materials have the phase sequence $\text{Iso} \rightarrow \text{Col}_h \rightarrow \text{Col}_{ho}/\text{Cr}$. The temperature range of the mesophase is much larger compared to the nonfluorinated porphyrins. Introducing fluorine atoms into the chains of self-assembling discotic LC porphyrin provides a structural change that supports and enhances the tendency towards uniform alignment and self-assembly. The homeotropic alignment is much easier to be obtained than previous synthesized non-fluorinated
porphyrins. The homogenous alignment was also obtained by shearing the texture at the temperature just below isotropic phase.

Optical properties of the fluorinated porphyrins were studied by UV-vis absorption and fluorescence. They were measured in solution and thin cells with or without the addition of PCBM. All target compounds have strong absorption at the Soret band in UV spectra and are quenched upon the addition of PCBM. Strong emissions were observed for fluorescence emission.

Further research on the device application is still under investigation.
Chapter 4

Fluorinated Intermediates---Acids

Part of this chapter is also available in “New mesogen with thermotropic cubic phase: 3,4,5-tris-(11,11,12,12,13,13,14,14,15,15,16,16-tridecafluoro-hexadecyloxy)-benzoic acid” X. Zhou, T. Narayanan, Q. Li, *Liquid Crystals* 2007, 34, 1243.

4.1 Introduction

A majority of nonconventional LCs is amphiphilic, i.e. the molecule is composed of at least two chemically different building blocks that are incompatible, one part is hydrophobic and the other is hydrophilic. Among the nonconventional LCs, the thermotropic cubic phases, which represent ordered supramolecular arrangements, are optically isotropic. These phases are attracting much interest due to their tremendous biological significance and potential application in drug delivery systems, etc, although the history of cubic phases dates from the first synthesis of nitrobenzyl carboxylic acids by Gray in the 1950s.\(^{70,71,72,73,74,75,76,77}\) Compared with the lyotropic cubic system, relatively few thermotropic compounds with isotropic cubic phases have been reported, although they have currently been recognized in a wider range of materials such as polyhydroxy molecules, dendritic molecules and metallomesogens; a cubic phase is often observed at relatively high temperatures.\(^ {78}\) In this chapter, we will investigate the benzoic
The intermediates 8 are benzoic acids and have oxygen-hydrogen bond. The carboxylic acid group allows for hydrogen atoms to easily attach to the oxygen atoms and form hydrogen bondings (Scheme 4.1). Based on similar benzoic acids, it is not surprising that a discotic mesophase is formed by hydrogen bonding. What is surprising is that, besides the discotic liquid crystalline phase, a cubic phase was found at the optically isotropic temperature. To the best of our knowledge, this is the first compound with the general structure of 3,4,5-tris(partially perfluorinated alkoxy)benzoic acids that exhibits a cubic phase.

Scheme 4.1 The scheme representation of hydrogen bonding for compound 8b.

4.2 Thermal Behavior of the Benzoic Acids 8
The thermal behavior of the fluorinated acids was investigated by DSC and POM and the results suggest that they all have a liquid crystalline phase (Fig. 4.1). In contrast, the nonfluorinated acids 2a and 2b don’t have a mesophase at all.

Fig. 4.1 Microscope textures under crossed polarizers of the fluorinated acids a) 8a, b) 8b, c) 8c at room temperature, d) 8d at 41.4 °C and e) 8e at room temperature.

Among the five acids, compound 3,4,5-tris (11,11,12,12,13,13,14,14,15,15,16,16 tridecafluorohexadecyloxy) benzoic acid 8b was selected for further studies. Compound 8b has a LC phase with an observable fan texture under crossed polarizers while its non-fluorinated analog T16 and corresponding methyl ester 7b show no indication of being mesogenic. The DSC thermograms and phase transitions of these three compounds (Fig. 4.2) are shown in Fig. 4.4 and Table 4.1.

It is not surprising that the methyl ester 7b does not have a liquid crystalline phase since the ester 7b lacks the capability of forming hydrogen bond. The non-fluorinated
analogue of 8b, T16 has the capability of forming hydrogen bond but still does not exhibit a liquid crystalline phase. This could be caused by the unique properties of the perfluorinated chains, which are more rigid, less miscible in organic solvent, and have a smaller steric bulk than the corresponding perhydrogenated alkanes that enhances the stability of the columnar and cubic phases.

In the DSC thermogram, there is only one transition peak from isotropic phase to crystal phase for T16 and 7b that appeared at 64.4 °C and 32.58 °C respectively. Crystalline textures were observed by cooling from the isotropic phase for T16 and 7b (Fig. 4.3g and h).

Fan textures were obtained after cooling fluorinated acid 8b from isotropic temperature. When the material 8b was heated up starting from room temperature, the fan texture under crossed polarizing microscope was maintained until it started to gradually disappear and turned complete black at 81 °C. No change to the optically isotropic phase was observed under the crossed polarized microscope with further heating up to 300 °C. There is a big transition peak at 214.32 °C with enthalpy of 17.62 J/g from the optically isotropic phase, which was later confirmed to be a cubic phase by small-angle X-ray diffraction (SAXD). On the second cooling at 153.50 °C, a small peak with the enthalpy of 2.02 J/g appeared which suggests a transition from one cubic phase to another cubic phase. When the temperature was cooled to 51.80 °C, the transition from cubic phase to hexagonal columnar phase transition occurred corresponding to the fan texture was observed from POM.
Fig. 4.2 Chemical structures of a) 8b, b) T16 and c) 7b.

Fig. 4.3 Microscope textures under crossed polarizers of 8b on heating, at a) 24 °C, b) 52 °C, c) 73 °C, d) transition from hexagonal columnar phase to isotropic cubic phase at 78 °C, e) 79 °C and f) 81 °C, g) crystal of T16 grown from isotropic phase at 42 °C, h) crystal of 7b grown on cooling from isotropic at 31 °C.
Fig. 4.4 DSC thermograms of a) T16, b) 7b, and c) 8b (heating: dark blue line; cooling: pink line).

Table 4.1 Phase transitions and transition enthalpy changes of 8b, T16 and 7b from DSC on cooling.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Transition temperatures (°C) and enthalpy changes (Jg⁻¹ in [ ] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>T16</td>
<td>Iso 64.4 [117.45] Cr</td>
</tr>
<tr>
<td>7b</td>
<td>Iso 32.58 [39.97] Cr</td>
</tr>
</tbody>
</table>

4.3 Synchrotron Small-Angle X-ray Diffraction Study
SAXD data done by Dr. Narayanan in France was used to verify the mesophases of $8b$. As mentioned before, when the sample was heated to 78 °C, the texture under crossed polarizers gradually became completely black. But the DSC and X-ray data confirmed that the cubic phase exists above that temperature. In order to characterize these phases better, SAXD patterns were recorded when the sample was cooled in steps from the isotropic phase at 250 °C. A similar sequence of phase changes with the DSC and POM results was observed in SAXD when the sample was heated at 1 °C/min. Fig. 4.5a shows that the isotropic to cubic phase transition occurs just above 200 °C. Upon cooling further, a hexagonal-like structure appears below 30 °C. In Fig. 4.5a, the pattern at 25 °C is recorded prior to heating the sample. Fig. 4.5b depicts evolution of the cubic phase as the temperature is decreased. When it is fully developed, the ratio of peak positions is $1: \sqrt{2}: \sqrt{3}: 2: \sqrt{5}: \sqrt{6}: \sqrt{7}: \sqrt{8}$ and the multiplicities of the peaks are consistent with a body centered cubic structure (space group Im3m). The cubic lattice parameter increases from 4.4 nm at 200 °C to 4.7 nm at 50 °C. This corresponds to a change in the nearest neighbor distance of 3.82 nm to 4.07 nm and it is consistent with the dimer size of molecule $8b$. 
Fig. 4.5 Powder small-angle X-ray diffraction pattern from 8b. a) On cooling the cubic phase appears at 200 °C with an increased lattice spacing at 50 °C; and then transform to hexagonal columnar phase below 30 °C. b) Evolution of the cubic phase while cooling the sample. The peak positions and multiplicities can be indexed to space group symmetry Im3m with lattice parameters 4.4 nm and 4.7 nm at 200 °C and 50 °C, respectively.

Below 30 °C, a hexagonal-like columnar phase with characteristic 1: √3: 2: √7: 3 peak positions appeared which is similar to the cubic to hexagonal transition observed in certain lyotropic systems. While heating the sample, the hexagonal phase can remain stable up to 70 °C, sometimes even with two different lattice spacings. The phase sequence of 8b, Iso→Cub→Colh, observed when cooling the sample from isotropic phase is more reproducible. The equilibrium hexagonal diffraction pattern in Fig. 4.5a corresponds to a lattice parameter of 4.6 nm. This means that the nearest neighbor distances are similar in both the cubic and hexagonal phases. The POM texture shown in Fig. 4.3 indicates this gradual transition from hexagonal to cubic phase when the sample is heated from room temperature. In contrast, the nonfluorinated analogue did not exhibit any interesting phase behavior by SAXD. Fig. 4.6 depicts the corresponding SAXD pattern of T16 recorded when cooling the sample from the isotropic phase. Detailed
investigations of phase transitions in these interesting liquid crystalline phases are in progress.

**Fig. 4.6** Small-angle X-ray diffraction pattern from T16 at 74 °C (isotropic phase), 72 °C (co-existence of isotropic and crystal phase) and 42 °C (crystal phase).

### 4.4 Conclusion

The perfluorinated benzoic acid 8b exhibits a very interesting phase sequence. This is the first compound with the general structure of 3,4,5-tris (partially perfluorinated alkoxy)benzoic acid that exhibits a cubic phase. The cubic phase is stable over a wide temperature range from about 200 °C to 30 °C on cooling, which makes it suitable for detailed investigations of phase transitions and potential applications. This research would provide new insight for self-assembling molecules into ordered superstructures via both perfluorinated chains and hydrogen bonds.
Chapter 5

Metalloporphyrins

5.1 Introduction

LC phases of porphyrin can be induced and enhanced by metal chelation. In the area of photovoltaic cells, researchers clearly want to resemble chlorophyll to have its light-harvesting and electron-transfer properties. The LC properties of this kind of metal-porphyrin complexes were first studied by Bruce’s group. Interestingly these researchers found that 5,15-bis(p-alkoxyphenyl)porphyrinatozinc (II) (Fig. 5.1) shows smectic B, E, and E’ phase (that is \( S_B \), \( S_E \) and \( S_{E'} \)). This is contradictory to the common belief that this kind of long chain disk-like molecules tend to show a columnar mesophase. Moreover, the metal can also affect the charge transport along the column and will change the electronic properties of materials. Metalation of porphyrins will also change the molecular energy and alter the absorption as well as photoemission spectrum. In order to investigate the effect of metalation on the phase behavior and charge mobility, zinc, copper and magnesium metal complexes of previously synthesized nonfluorinated and fluorinated porphyrins were prepared and studied.

![Fig. 5.1 Structure of metalloporphyrin complex showing \( S_B \), \( S_E \) and \( S_{E'} \) phase.](image)

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5.2 Synthesis of Metalloporphyrins

Zn (II), Cu (II) and Mg (II) porphyrin complexes were synthesized and characterized. The metalation of the porphyrins was carried out through a one-step reaction using the metal salts under mild conditions. The zinc and copper metallated porphyrins were obtained from the metal acetate salt reacting with the porphyrin in methylene chloride and methanol at room temperature (Scheme 5.1). To synthesize the magnesium metallated porphyrins, attempts were made to react MgBr₂ with porphyrin. Unfortunately, the insertion of magnesium into porphyrin by this method was unsuccessful. Reaction optimization studied by Woodford et al.⁸³ shows that up to 40 equivalents of MgBr₂ was required in order to get a fairly good yield and if only 10 equivalents of MgBr₂ was added, the reaction proceeds poorly. MgBr₂(OEt)₂ and MgI₂ seem to be the better magnesium reagents for the magnesium chelates of the porphyrins. Finally, MgI₂ was chosen as the reagent to convert porphyrin to the magnesium chelate. Reactions were performed with 10 equivalents of MgI₂ and 20 equivalents of the base triethylamine at room temperature in methylene chloride.

While Cu complexes have generally a low affinity for extra ligands, the chelates with Mg and Zn readily have one more ligand to form pentacoordinated complexes.⁸⁴ However, the structure can be confirmed by matrix assisted laser desorption mass spectrometry (MALDI).⁸⁵ The Cu complexes are paramagnetic and cannot be analyzed by NMR spectroscopy,⁸⁶ but the target Cu complex compounds were confirmed by the elemental analysis. For some compounds, a small peak was observed except for the major peak in mass spectra. It’s unclear whether this peak comes from fragment or impurity.
However, all the metal complexes were fully identified by proton and carbon NMR, mass spectroscopy and elemental analysis confirming the purity.

\[\text{Scheme 5.1 Synthetic scheme of the porphyrin metal complexes.}\]
5.3 Zinc Complexes

5.3.1 Thermal Behavior

The thermal behavior of the zinc complexes was identified by DSC and POM studies. 5 µm cells were used for the POM investigation. From the experimental results, when the cooling rate is 0.2 °C/min, a typical batonnet texture was formed immediately below the isotropic temperature for nonfluorinated zinc complexes (Fig. 5.2). It took about 10 °C for the compounds to complete the formation of the texture. If the cooling rate is increased to 2 °C/min before the complete texture is formed, very small batonnets appeared (Fig. 5.2d). Once the texture is formed, no big changes were observed through room temperature. This batonnet texture is typical for smectic phases and is quite different from the fan texture of the metal free porphyrin. The reason could be that the zinc metal induces different LC phase (smectic phase) to the porphyrins. The exact mesophase has not yet been confirmed by X-ray data.
Fig. 5.2 Microscope textures under crossed polarizers of 10a at a) 127 °C, b) 114 °C, 10b at c) 107 °C and d) 88 °C.

Taking compound 10b as an example, upon heating from the crystal phase, it went to the LC phase at the temperature of 7 °C from DSC on second heating, while the POM texture stays almost the same. When the sample was heated up to 112 °C, the phase transitioned from mesophase to isotropic phase and the texture went to completely black under POM. During the cooling sequence, the needle like batonnet texture was formed from the isotropic phase at the temperature of 92 °C. Upon further cooling to 2 °C, the crystal phase was formed while no obvious change observed under POM. The phase
sequence cooling from isotropic can be summarized to be: \textbf{Iso}→\textbf{P}→\textbf{Cr} where \textbf{P} stands for the unknown mesophase.

\textbf{Fig. 5.3} DSC thermogram of zinc complex 10b (heating: dark blue line; cooling: pink line).

Unlike nonfluorinated metalloporphyrins, the perfluorinated metalloporphyrins exhibit similar phase behavior with their corresponding metal free porphyrins. The fan textures (Fig. 5.4) appeared after cooling from the isotropic phase which is similar to what we found in its metal free porphyrin. The homeotropic alignment was hard to get even at the slow cooling rate of 0.2 °C/min. This alignment effect might be attributed to the insertion of metal that leads to the disorder of π-π packing between the discs through the columns. The DSC spectra of zinc complexes also show similar transition peaks with the metal free porphyrins which strongly suggest the zinc complexes possess discotic columnar phases.
Fig. 5.4 Microscope textures under crossed polarizers of a) **10c** at 160 °C and b) **10d** at 25 °C.

Taking **10c** as an example of fluorinated metalloporphyrins, on the cooling sequence, the columnar LC phase was formed from the isotropic phase at 198 °C with a latent heat of 1.475 J/g. Fan textures appeared under POM during this transition. With further cooling to 128 °C, a second peak in the DSC occurred with the latent heat of 3.494 J/g which is similar to metal free fluorinated **9d** at 125 °C. This similarity suggests that the second transition is from columnar LC phase to the more ordered columnar LC phase. No big change in the texture was observed once it was formed through room temperature. It’s clear from the DSC that with the metal in the porphyrin core the isotropic temperature decreased by about 20 °C. The transition temperatures and enthalpies of **10c** and **9d** are listed in Table 5.1 for comparison.

In conclusion, the nonfluorinated and fluorinated zinc complexes show different phase behaviors. For **10a** and **10b**, they seem to have only one mesophase which shows a batonnet structure and is unidentified. The phase sequence can be simply presented as: **Iso→P→Cr** where **P** stands for unknown phase. For perfluorinated compounds **10c** and
10d, similar phase sequence to their metal free porphyrins was observed: 
Iso → Col\textsubscript{h} → Col\textsubscript{ho} → Cr. All the mesophases were not yet been confirmed by X-ray data.

![Fig. 5.5 DSC thermogram of zinc complexes a) 10c and metal free porphyrin b) 9d](image)

(heating: dark blue line; cooling: pink line).
Table 5.1 Phase transition and transition enthalpy changes of 9d and 10 from DSC on cooling.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Transition temperatures (°C) and enthalpy changes (Jg⁻¹ in [ ])</th>
</tr>
</thead>
<tbody>
<tr>
<td>9d</td>
<td>Iso: 221.64 [1.228] Colh: 123.45 [2.017] Colho Cr</td>
</tr>
<tr>
<td>10a</td>
<td>Iso: 112.57 [2.53] P: 2.18 [26.12] Cr</td>
</tr>
<tr>
<td>10b</td>
<td>Iso: 92.38 [7.28] P: 2.18 [26.12] Cr</td>
</tr>
<tr>
<td>10c</td>
<td>Iso: 202.12 [1.81] Colh: 134.10 [7.49] Colho Cr</td>
</tr>
<tr>
<td>10d</td>
<td>Iso: 190.44 [0.46] Colh: 105.83 [1.75] Colho Cr</td>
</tr>
</tbody>
</table>

5.3.2 Optical Properties

The UV-vis spectra of zinc complexes for both nonfluorinated and perfluorinated porphyrins are similar to the metal free porphyrins. Compound 10a as a representative is shown below in Fig. 5.6. The Soret bands have a small shift while the Q bands have big shifts compared to their corresponding metal free porphyrins. Instead of four absorption Q bands in metal free porphyrins, metal complexes have only one Q band at the wavelength near 420 nm. The molar absorption coefficients for the highest absorption wavelength and the Q band are listed in Table 5.2.

Table 5.2 Molar absorption coefficients of the Soret bands and Q bands for compounds 10.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Maximum Absorption Wavelength (nm)</th>
<th>Absorption Coefficient (10⁵ M⁻¹ cm⁻¹)</th>
<th>Q band (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10a</td>
<td>420</td>
<td>5.1</td>
<td>549</td>
</tr>
<tr>
<td>10b</td>
<td>418</td>
<td>5.6</td>
<td>549</td>
</tr>
<tr>
<td>10c</td>
<td>420</td>
<td>5.4</td>
<td>549</td>
</tr>
<tr>
<td>10d</td>
<td>421</td>
<td>5.4</td>
<td>549</td>
</tr>
</tbody>
</table>
At the excitation wavelength of 420 nm, the emission peaks appeared at 594 nm and 642 nm. The fluorescence spectra of compounds 10 have only a slight difference compared to the metal free analog, the emission spectra are blue shifted and the emission intensity at the left side becomes lower than the right side.
In summary, the UV-vis spectra exhibit strong absorption at around 420 nm and the fluorescence spectra show strong emission peaks at about 590 and 640 nm. The optical properties of all the compounds of 10 are similar to the metal free porphyrins.

5.4 Copper Complexes

5.4.1 Thermal Behavior

The thermal behavior of copper complexes was investigated by DSC and POM study. In order to obtain a nice texture, 5 µm cells were used for POM investigation as before. Basically, the thermal behaviors of copper compounds exhibit similar phenomena with the zinc complexes. A batonnet texture was formed for nonfluorinated copper complexes 11a and 11b, and a fan texture was obtained for perfluorinated copper complexes 11c and 11d. The DSC thermograms are represented by 11b and 11c in Fig. 5.9 for nonfluorinated complexes and perfluorinated complexes respectively.

For 11b, the batonnet textures appeared during the transition from isotropic to mesophase at 101.50 °C with a latent heat of 9.84 J/g on DSC. Upon further cooling the textures stayed almost the same while the transition from mesophase to crystal phase appeared at 2.26 °C with an enthalpy of 25.07 J/g.

For fluorinated complex 11c, the transition to mesophase from isotropic occurred at 209.81 °C with enthalpy of 1.80 J/g. Small fan textures were observed during this transition under POM. Unlike zinc metalloporphyrins, large homeotropic areas were obtained by cooling the sample slowly at the rate of 2 °C/min (Fig. 5.8a and c). The second transition from what is assumed to be a Colh phase to more ordered Colho phase appeared at 126.52 °C with an enthalpy of 5.01 J/g. The columnar LC phase to crystal
phase transition was not observed even when cooled to -25 °C. The mesophases of compounds 11 need to be confirmed by X-ray.

Fig. 5.8 Microscope textures under crossed polarizers of a) 11a, b) 11b, c) 11c and d) 11d at room temperature.
Fig. 5.9 DSC thermograms of a) 11b and b) 11c (heating: dark blue line; cooling: pink line).

Table 5.3 Phase transitions and transition enthalpy changes of 11 from DSC cooling.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Transition temperatures (°C) and enthalpy changes ($\text{J g}^{-1}$ in [ ] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>11a</td>
<td>Iso 116.98 [7.76] P Cr</td>
</tr>
<tr>
<td>11b</td>
<td>Iso 101.50 [9.84] P 2.26 [25.07] Cr</td>
</tr>
<tr>
<td>11c</td>
<td>Iso 209.81 [1.80] Col$<em>h$ 126.52 [5.01] Col$</em>{ho}$ Cr</td>
</tr>
<tr>
<td>11d</td>
<td>Iso 216.75 [1.77] Col$<em>h$ 117.87 [4.46] Col$</em>{ho}$ Cr</td>
</tr>
</tbody>
</table>
5.4.2 Optical Properties

The UV-vis spectra of all the copper complexes 11 are similar to metal free porphyrins except for a shift in the Q bands. The molar absorption coefficients and the Q bands are listed in Table 5.4.

Table 5.4 Molar absorption coefficients of the Soret bands and Q bands for compounds 11.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Maximum Absorption Wavelength (nm)</th>
<th>Absorption Coefficient ( \times 10^5 ) M(^{-1})cm(^{-1})</th>
<th>Q band (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11a</td>
<td>416</td>
<td>4.9</td>
<td>540</td>
</tr>
<tr>
<td>11b</td>
<td>419</td>
<td>5.4</td>
<td>539</td>
</tr>
<tr>
<td>11c</td>
<td>416</td>
<td>5.4</td>
<td>540</td>
</tr>
<tr>
<td>11d</td>
<td>416</td>
<td>5.6</td>
<td>540</td>
</tr>
</tbody>
</table>

There is almost no fluorescence emission at the excited wavelength for all the copper complexes. It seems that the fluorescence is completely quenched by the copper insertion. As an example, the metal free porphyrin 9d and copper complex 11c are used for comparison in the same concentration (Fig. 5.10). The fluorescence spectrum of 9d in methylene chloride has two emission bands at 650 nm and 716 nm, while the intensity at 650 nm is higher than the other band. At the same concentration, the emission of 11c is completely quenched compared to 9d. Normally fluorescence quenching is caused by photoinduced electron transfer from porphyrins. The detailed mechanism for the photoinduced electron transfer process of the system still remains unclear.
Fig. 5.10 Fluorescence spectra of a) 9d (c=3.7 µM) and b) 11c (c=3.7 µM) in methylene chloride solution.

5.5 Magnesium Complexes

5.5.1 Thermal Behavior
The thermal behavior of magnesium complexes were investigated by DSC and POM. 5 µm cells were used for POM study as before. DSC patterns show that a very broad peak emerges instead of normal sharp peak at the second transition of nonfluorinated magnesium complexes (Fig. 5.11) on cooling at the phase transition supposed to be mesophase to crystal phase. The phase transition temperatures and enthalpy changes are listed below in Table 5.5.
Fig. 5.11 DSC thermogram of porphyrin magnesium complexes a) 12b and b) 12d (heating: dark blue line; cooling: pink line).

Table 5.5 Phase transitions and transition enthalpy changes of 12 from DSC on cooling.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Transition temperatures (°C) and enthalpy changes (Jg(^{-1}) in [ ] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>12a</td>
<td>Iso 67.3 [0.58] P -11.7 [17.10]</td>
</tr>
<tr>
<td>12b</td>
<td>Iso 77.0 [0.69] P 12.5 [38.50]</td>
</tr>
<tr>
<td>12c</td>
<td>Iso 199.1 [1.23] P</td>
</tr>
<tr>
<td>12d</td>
<td>Iso 182.3 [0.49] P</td>
</tr>
</tbody>
</table>
The color of the magnesium complexes is green. Though it’s a little bit dark under POM, small fan textures can still be seen (Fig. 5.12). Taking compound 12b as an example, upon cooling from isotropic phase, the first peak appeared at 77 °C with an enthalpy of 0.69 J/g. The fan texture was gradually formed under POM during this transition. With further cooling, a broad peak was observed at 12.5 °C with an enthalpy of 38.5 J/g supposed to be the transition from mesophase to crystal phase. The texture remained unchanged through room temperature.

Fig. 5.12 Microscope textures under crossed polarizers of a) 12b and b) 12d at room temperature.

5.5.2 Optical Properties

The absorptivity of magnesium complexes was extremely low so that it can even be ignored. The molar absorption coefficients are calculated and listed in Table 5.6.
Table 5.6 Molar absorption coefficients of the Soret bands for compounds 12.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Maximum Absorption Wavelength (nm)</th>
<th>Absorption Coefficient (10^5\text{ M}^{-1}\text{cm}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>12a</td>
<td>428</td>
<td>-</td>
</tr>
<tr>
<td>12b</td>
<td>426</td>
<td>-</td>
</tr>
<tr>
<td>12c</td>
<td>427</td>
<td>0.2</td>
</tr>
<tr>
<td>12d</td>
<td>427</td>
<td>0.2</td>
</tr>
</tbody>
</table>

While the UV absorbance was extremely low, the fluorescence emission was very strong. All the magnesium complexes exhibit a similar fluorescence emission. Spectrum of 12a is presented below as an example in Fig. 5.13. The emission wavelengths at the excitation wavelength of 428 nm are 610 nm and 664 nm and the emission intensity at 610 nm is stronger than 664 nm. Further characterization is in progress.

![Fluorescence spectrum of 12a in methylene chloride.](image)

Fig. 5.13 Fluorescence spectrum of 12a in methylene chloride.

5.6 Conclusion
The Zn, Cu and Mg complexes of both nonfluorinated and fluorinated porphyrins were synthesized. Their chemical structures were well identified by $^1$H NMR, $^{13}$C NMR, IR, mass spectroscopy and elemental analysis.

The mesophases of the metalloporphyrins were identified by POM and DSC thermogram. The POM textures of nonfluorinated zinc and copper complexes were a batonnets which is different from fan texture of other complexes. The phase sequence for nonfluorinated complexes can be summarized as Iso→P→Cr. And the fluorinated complexes exhibit the phase sequence: Iso→Col$_h$→Col$_{ho}$→Cr. All the mesophases do not have X-ray confirmation yet.

Optical properties of zinc porphyrin complexes were similar to the previous porphyrins studied. The UV-vis absorption of copper complexes was also similar to other porphyrin compounds while the fluorescence was completely quenched. Interestingly, there was almost no absorption for magnesium complexes but the fluorescence was as strong as other porphyrins.

Only fluorinated copper complexes show strong tendency toward homeotropic alignment. The fluorescence quenching phenomena observed from 11c and 11d indicates that photoinduced electron transfer might occur in intermolecular system. Thus, fluorinated copper complexes might be good candidates for PV materials.
Chapter 6

Chiral Porphyrins

6.1 Introduction

Chirality was defined by Lord Kelvin about one century ago. It is derived from the Greek word *cheir*, which means hand-like. The hand is chiral because it cannot be superimposed with its mirror image.

Chiral compounds with liquid crystalline phases typically show very interesting optical and electro-optic properties. Introducing an optically active element into a LC often lead to polar structures and periodic structures with mesoscale dimensions. Researchers have already investigated widely on the introduction of chirality into nematic and smectic LCs.

Discotic LCs can form columnar supramolecular structures by π-stacking. Introducing chirality into the superstructure is a relatively new area called supramolecular chirality which combines supramolecular chemistry and molecular chirality. Meisenheimer and Witte prepared the first helicenes-helical molecules comprised of ortho-fused aromatic rings but their chirality wasn’t discovered until 1955 when Newman pointed it out. Since then, researchers found that nature has demonstrated a lot of molecular self-organization into helical architectures such as the α-helix of polypeptides and the double helix of DNA, where hydrogen bonding, stacking interactions and hydrophobic effects are the driving forces of the formation of these helices. Chiral dendrimers are considered as good
candidates for the investigation of chirality at the macromolecular level.\textsuperscript{93} It’s reasonable to expect that if this kind of helix stacking could be introduced into columnar LCs, the normal stack of columnar LCs could stack in a helical manner (Fig. 6.1).\textsuperscript{94} The helical superstructures are found to have interesting linear optical and nonlinear optical properties, electrooptical behavior, etc.

\begin{center}
\textbf{Fig. 6.1} Schematic representation of a supramolecular helical structure.
\end{center}

Since the introducing of chirality into a columnar LC could result in different interesting property changes such as nonlinear optical property, it would be interesting to introduce the chirality into our porphyrin system in order to enlarge the properties of our columnar LCs. Based on previous experiences, porphyrins synthesized via intermediate porphyrin A (see page 25) with moderate functional chains, show columnar LC phases. Thus, in the simplest way, we introduce the chiral moiety into the chains in order to obtain the supramolecular chirality.

\textbf{6.2 Synthesis of Chiral Porphyrins}
To synthesize different chiral porphyrins, the porphyrin core was kept intact while a chiral moiety, linked through the benzoic acid to the porphyrin core, was modified with different functional groups and alkyl lengths. Three kinds of chiral porphyrins with a chiral moiety at different places were successfully synthesized (Fig. 6.2).

**Fig. 6.2 Chemical structures of target compounds 18, 24 and 26.**
6.2.1 Synthesis of the Chiral Porphyrins

The intermediate 13 was synthesized by reacting methyl tris-3,4,5-hydroxy benzoate with bromo substituted alcohol via Williamson ether formation in DMF. The bromo substituted alcohol was added dropwise to the dilute solution of benzoate in DMF. The crude compound was purified by flash chromatography to afford white solid in about 30% yield. Then the benzoic acid 14 was obtained by hydrolysis from the benzoate 13 with high yield.

\[
\text{HO} \quad \text{O} \quad \text{O} \\
\text{HO} \quad \text{O} \quad \text{O} \\
\text{HO} \quad \text{O} \quad \text{O} \\
\text{HO} \quad \text{O} \quad \text{O} \\
\text{HO} \quad \text{O} \quad \text{O}
\]

\[
\text{+} \quad \text{HO} \quad \text{R} \quad \text{Br} \\
\text{DMF, K}_2\text{CO}_3 \\
80^\circ\text{C} \\
\text{HO} \quad \text{O} \quad \text{O} \\
\text{HO} \quad \text{O} \quad \text{O} \\
\text{HO} \quad \text{O} \quad \text{O} \\
\text{HO} \quad \text{O} \quad \text{O} \\
\text{HO} \quad \text{O} \quad \text{O}
\]

13a: R=C\text{\textsubscript{11}}H\text{\textsubscript{22}}
13b: R=C\text{\textsubscript{6}}H\text{\textsubscript{12}}

\[
\text{HO} \quad \text{R} \quad \text{O} \\
\text{HO} \quad \text{R} \quad \text{O} \\
\text{HO} \quad \text{R} \quad \text{O} \\
\text{HO} \quad \text{R} \quad \text{O} \\
\text{HO} \quad \text{R} \quad \text{O}
\]

14a: R=C\text{\textsubscript{11}}H\text{\textsubscript{22}}
14b: R=C\text{\textsubscript{6}}H\text{\textsubscript{12}}

Scheme 6.1 Synthetic scheme of intermediate 13 and 14.

Then (S)-(+)2-methylbutyryl chloride C\text{\textsubscript{1}} was made to attach to the resulted benzoic acid 14. Unfortunately, this procedure was not successfully performed. The (S)-(+)2-methylbutyryl chloride C\text{\textsubscript{1}} was synthesized by reacting with its corresponding acid (S)-(+)2-methylbutyric acid with oxalyl chloride under air free condition. After 3 hours,
when the reaction was completed which was confirmed by IR, the mixture was distilled under reduced pressure at the temperature of 30 °C to get rid of the excess oxalyl chloride. The resulting crude C1 was added dropwise to the solution of 14 and Et3N in anhydrous THF at 0 °C. However, this reaction didn’t go through as expected to afford the ester C2. The reasons might be that 1) the oxalyl chloride still exists in the reaction and made the reaction more complicated 2) anhydride might be formed by C1 reacting with the benzoic acid.

Scheme 6.2 Synthetic scheme of an unsuccessful procedure.

Because of the unsuccessful reaction above, the procedure was changed to another synthetic route. In order to avoid the intermolecular reaction occur when attaching the benzoic acid to the porphyrin core, the terminal chain of compound 14 was protected by dihydro-pyran (DHP). This THP protection reaction was conducted in the presence of
anhydrous THF with catalytic amount of p-TsOH at room temperature for 10 hours. The yellow oil products 15 were isolated by column chromatography in good yield.

![Diagram of synthetic scheme of THP protected acids 15.]

**Scheme 6.3** Synthetic scheme of THP protected acids 15.

The THP protected compound was reacted to the porphyrin core A via ester formation to afford the intermediate 16 in high yield. Then the THP protected porphyrins were deprotected by p-TsOH in MeOH refluxing for 1 hour. The resulting crude compounds 17 were purified by column chromatography using 20% MeOH and 30% EtOAc in hexane as eluent. The final step was taken by reacting compounds 17 with the commercial available (S)-(+-)2-methylbutyric acid to afford the target compounds 18.

Compounds 18a and 18b were identified by $^1$H NMR and $^{13}$C NMR. Taking compound 18a as an example, proton NMR spectrum shows that in the aromatic region, there are peaks at 7.61 ppm (singlet), 7.64 ppm (doublet) and 8.29 ppm (doublet), 8.96 ppm (singlet). Among them, 7.61 ppm singlet and 8.96 ppm singlet correspond to the two protons on the porphyrin ring. The fact that these two peaks are singlet proves that our molecule is a symmetrical molecule with the same structure on four different directions. The two doublet peaks at 7.64 ppm and 8.29 ppm correspond to the two benzene protons.
that are coupling to each other \((J = 8.4\text{Hz})\) (Fig. 6.3). The fact that there is only one doublet also confirms that our molecule is a symmetrical molecule. The peak 176 ppm in carbon NMR spectrum proves that there is only one carbonyl carbon present, which can exclude the possibility of the zero and incomplete unsymmetry esterification (Fig. 6.4). If we compared the nonaromatic proton NMR spectrum at 3-5 ppm region for 17a and 18a, 17a has the peaks at 3.65 ppm (multiplet) and 4.16 ppm (multiplet) and 18a has the peaks at 4.08 ppm (multiplet) and 4.16 ppm (multiplet) for 18a. It’s clear that the proton peak at 4.16 ppm is the same, which represents the aromatic ether proton far away from the reaction site. And the other proton is significantly shifted to the low field (from 3.65 ppm to 4.08 ppm), which represents the ether proton near the esterfication sites. Because there is no proton appeared in 3.65 ppm, all the alcohols no longer existed, which means all of them were converted to ester. So this compound should have 12 esterifications happened. So NMR spectra confirm that we have the wanted product.
Scheme 6.4 Synthetic scheme of THP protected porphyrins 16. 

16a: R=C_{11}H_{22}  
16b: R=C_{6}H_{12}
Scheme 6.5 Synthetic scheme of intermediate 17 and target porphyrins 18.
Fig. 6.3 Proton NMR spectrum of compound 18a.
In addition to the chiral moiety at the terminal position of the side chain, we attached the chiral part to the middle of the chains. (R)-(-)-3-Bromo-2-methyl-1-propanol was reacted with methyl 3,4,5-trihydroxy benzoate via Williamson ether formation reaction in acetone to produce the benzoate with chiral moiety 19 followed by the hydrolysis to afford benzoate acid 20. It is worthwhile to mention that acetone was used as the solvent instead of DMF due to poor yields in DMF.
Scheme 6.6 Synthetic scheme of chiral benzoate 19 and benzoic acids 20.

The intermediate acid 20 was protected by DHP under the same condition with the first approach to produce the THP protected benzoate acid 21. The porphyrin core then reacted with 21 to afford the THP protected porphyrin 22 by ester formation.
Scheme 6.7 Synthetic scheme of THP protected acid 21 and target 22.
The compound 22 was deprotected by p-TsOH to afford 23 followed by reacting with alkyl acid to give the target product 24.

Scheme 6.8 Synthetic scheme of deprotected porphyrin 23 and target compound 24.

In this approach, the chiral moiety was connected with the alkyl chains via an ester linkage. Considering the ester at the middle of the chains might cause the disorder of the molecular packing, we change the ester group to ether connection by the following two
steps. The compound 20 was reacted with the 1-bromo-tridecane by sodium hydride in anhydrous DMF via ether formation to get compound 25. It’s essential to keep the reaction under N₂ to avoid the moisture since NaH is sensitive to water. The resulting compound 25 was then reacted with the porphyrin core to give the target compound 26. This target compound was identified by NMR. The ¹H NMR spectrum of compound 26 shows that in the aromatic region, there are peaks at: 7.61 ppm (singlet), 6.77 ppm (doublet), 8.27 ppm (doublet) and 8.95 ppm (singlet). Among them, the peak at 8.95 ppm corresponds to the eight protons on the porphyrin ring. This peak as a singlet clearly demonstrates that the molecule is highly symmetrical, which means the four phenol groups on porphyrin were either all reacted or none was reacted. The peaks at 6.77 ppm and 8.27 ppm represent two groups of protons on the phenol rings attached directly to porphyrin. The peak at 7.61 ppm corresponds to the aromatic protons from the chiral segment. The presence of this proton proves that the esterification occurred. Together with information we obtained from 8.95 ppm, we can conclude that all four phenols attached to porphyrin were esterified. This is also confirmed by the fact that the peak at 7.61 ppm from compound 26 is shifted to the low field from 7.33 ppm from compound 25 because of the stronger inductive effect of ester groups to carboxylic acid groups. On the other hand, ¹³C NMR spectrum shows that there is only one carbonyl carbon at 165.12 ppm, which is in the range of conjugated carbonyls. This also confirms our molecule is symmetrical. Above all, together with TLC, compound 26 is the desired product.
Scheme 6.9 Synthetic scheme of chiral benzoate acid 25 and target compound 26.
6.3 Thermal Behavior of Chiral Porphyrins

The thermal behaviors of chiral porphyrins were studied by POM and DSC. Among the target compounds only compounds 18 seem to have LC phases. The DSC thermograms of 18 and the phase transition enthalpies are shown in Fig. 6.5 and Table 6.1.
Fig. 6.5 DSC thermograms of a) 18a and b) 18b (heating: dark blue line; cooling: pink line).

Table 6.1 Phase transitions and transition enthalpy changes of 18a and 18b from DSC on cooling.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Transition temperatures (°C) and enthalpy changes (Jg⁻¹ in [ ] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>18a</td>
<td>Iso 67.0 [1.97] P 52.8 [7.68]</td>
</tr>
<tr>
<td>18b</td>
<td>Iso 119.6 [3.00] P₁ 93.6 [11.24] P₂ 54.8 [3.58]</td>
</tr>
</tbody>
</table>
Red birefringence appeared when the sample 18a was cooled from the isotropic phase under crossed polarizing microscope. Fig. 6.6 shows that when 18a was heated to 74 °C, the birefringence gradually disappeared and went to isotropic at 77 °C under POM. The birefringence reappeared at 38 °C cooling from isotropic phase which lasted through room temperature.

![Fig. 6.6 Microscope textures under crossed polarizers of 18a during heating sequence](image)

For chiral porphyrin 18b, batonnet textures characteristic of a smectic phase were obtained during slow cooling from isotropic phase. The texture began disappearing at about 113 °C and became completely black at 120 °C. By cooling from isotropic temperature at the rate of 0.2 °C/min, batonnet textures appeared at 95 °C on POM. Upon
further cooling, the texture remained unchanged through room temperature. Further X-ray confirmation for phase identification is needed.

Based on the POM texture, no columnar phase was observed for compounds 18. This might be attributed to the introduction of chiral chains that perturb the formation of the columnar phases.

Fig. 6.7 Microscope textures under crossed polarizers of 18b during heating sequence a) 113 °C, b) 120 °C (isotropic), and on cooling c) 95 °C, d) 92 °C and e) 35 °C.

6.4 Optical Properties

Compound 18a and 18b exhibit similar optical properties. Taking 18a as a representative, it has strong absorption at the wavelength of 416 nm. The molar absorption coefficients are calculated and listed in Table 6.2. At the exciting wavelength of 416 nm, the fluorescence emission band appeared at 652 nm and 715 nm (Fig. 6.9).
Table 6.2 The molar absorption coefficients of the Soret bands for compounds 18.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Maximum Absorption Wavelength (nm)</th>
<th>Absorption coefficient ((10^5 \text{ M}^{-1}\text{cm}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>18a</td>
<td>416</td>
<td>5.7</td>
</tr>
<tr>
<td>18b</td>
<td>416</td>
<td>5.7</td>
</tr>
</tbody>
</table>

Fig. 6.8 UV-vis spectrum of 18a.

Fig. 6.9 Fluorescence spectrum of 18a.
6.5 Conclusion

Chiral porphyrins 18, 24 and 26 were synthesized and identified by $^1$H NMR, $^{13}$C NMR and IR. Chiral porphyrins 18 seem to have the LC phase but do not show the desired columnar phase. No typical texture was observed for 18a and batonnet texture was obtained for 18b. Both 18a and 18b show strong UV absorption and are highly fluorescent.
Chapter 7

Experimental Details

7.1 Materials and Methods

All chemicals and solvents were purchased from commercial suppliers and used without further purification. $^1$H NMR and $^{13}$C NMR spectra were recorded on either Varian 200 MHz NMR or a Bruker AVANCE 400 magnetic resonance spectrometer. Chemical shifts are in $\delta$ units (ppm) with the residual solvent peak as the internal standard. The coupling constant ($J$) is reported in hertz (Hz). NMR splitting patterns are designed as follows: s, singlet; d, doublet; t, triplet; and m, multiplet. Column chromatography was carried out on silica gel (60-200 mesh). Analytical thin layer chromatography (TLC) was performed on commercially coated 60 mesh F254 glass plates. Spots were rendered visible by exposing the plate to UV light. Elemental analysis was performed by Robertson Microlet Inc. Infrared FT-IR spectra were recorded with a KBr pellet.

Mass spectrum was taken by Mass Spectrometry & Proteomics Facility of Ohio State University. Bruker Reflex III MALDI-TOF mass spectrometer was used for the analysis of synthesized materials. Matrix-assisted laser desorption/ionization which is abbreviation for MALDI is a soft ionization technique used in mass spectrometry, allowing the analysis of biomolecules and large organic molecules. It is most similar in
character to electrospray ionization although it causes many fewer multiply charged ions.\textsuperscript{95}

The thermal behaviors of these compounds were studied by DSC and POM on untreated glass slides and cells. Textures and transition temperatures were observed by optical microscopy using a Leitz polarizing microscope in conjunction with a Mettler FP2 temperature controller. Calorimetric measurements were performed in a Perkin Elmer DSC using indium as a standard calibration.

Simple cells were fabricated by the following procedure. The ITO coated glass was cut into \(1 \times 1\) square inch pieces. They were then cleaned by the ultrasonic bath with the aid of heat at about 50 °C for 20 minutes and rinsed with isopropanol. The cleaned glasses were put into an oven and heated to 80 °C for 20 minutes. Then the dried glass substrates were assembled using NOA65 with spacers at the four corners. The monomer NOA65 was cured with 30 mW/cm\(^2\) intensity, 365 nm ELC4000 UV light for 5 minutes.

Antiparallel alignment cells were made by spin coating two clean ITO substrates with PI 2555 polyimide solution at the speed of 2500 rpm for 20 second. The substrates were then baked for about 2 minutes at 90 °C to get rid of solvent and then put into an oven at 275 °C for one hour. After removal from the oven, the glasses were rubbed and assembled in an antiparallel direction.

The quartz plates are 20mm x 20mm x 1mm. The quartz cells were cleaned in ultrasonic bath and assembled by the epoxy.
The UV-vis spectra were taken by a Perkin Elmer Lamda 19 spectrometer. Samples were prepared by dissolving in methylene chloride and measurements were done in standard quartz cuvettes of 1.0 cm path-length.

Fluorescence spectra were collected in methylene chloride on a Cary Eclips fluorescent spectrometer apparatus in a 1 cm cuvette. The excitation wavelengths are the maximum absorbance wavelengths in the UV-vis spectrum.

For the synchrotron X-ray diffractions (XRDs) on the homeotropic aligned thin films, the samples were sandwiched between 50 μm thick bare glass plates with an 8.0 μm gap and exposed to 50 μm × 50 μm size synchrotron X-ray beam of the Advanced Photon Source (APS) at Argonne National Laboratory (Midwestern University Collaborative Access Team’s facilities on Sector 6). The glass cells were slowly cooled down from isotropic to mesophase in order to obtain the homeotropically aligned textures. The sample cell was mounted inside a Hot Stage that controlled the sample temperature to ±0.02 °C. An X-ray wavelength of 0.7653 Å was used. The diffraction patterns were recorded at different temperatures during the cooling from isotropic phase using a high resolution Mar3450 area detector placed at a distance of 506.2 mm from the cell. For the synchrotron X-ray diffractions (XRDs) on unaligned powder sample, samples were sandwiched by Kapton films. The samples were exposed to the 200 μm × 200μm size synchrotron beam with 0.7653 Å wavelength. The diffraction patterns were recorded using a high resolution Mar3450 area detector placed at a distance of 518.5 mm from the sample. The recorded XRD patterns were analyzed using “FIT2D” software developed by A. P. Hammersley of the European Synchrotron Radiation Facility.
Small-angle X-ray diffraction (SAXD) experiments for fluorinated intermediate acid were carried out at the European Synchrotron Facility, Grenoble, France. Samples were contained in thin X-ray capillaries which were flame sealed in the nitrogen atmosphere. The temperature of the capillary was varied in steps using a Linkam heating stage. The normalized two dimensional diffraction patterns were azimuthally averaged to obtain the intensity, I(q), as function of scattering vector (q).

7.2 Experimental Details for Chapter 2

**Methyl 3,4,5-tris-tridecyloxy-benzoate (1a)**

A mixture of methyl 3,4,5-trihydroxybenzoate (1.03 g, 5.64 mmol), anhydrous potassium hydroxide (3.51 g, 25.36 mmol) and 1-bromotridecane (4.90 g, 18.60 mmol) in 25 ml DMF was heated to 70°C under stirring for 18 hrs. The reaction mixture was extracted with methylene chloride and water. The organic layer was washed three times with brine, dried over anhydrous magnesium sulfate and filtered. The solvent was evaporated. The residue was purified by flash chromatography using 4% ethyl acetate in hexane as eluent to afford the product as a white solid in 78% yield. m.p. 41.5 °C.

$^1$H NMR (400 MHz, CDCl$_3$): δ 0.88 (t, 9H, $J$=7 Hz), 1.30 (m, 54H), 1.47 (m, 6H), 1.70 (m, 6H), 3.89 (s, 3H), 4.01 (m, 6H), 7.25 (s, 2H)

$^{13}$C NMR (100 MHz, CDCl$_3$): 14.11, 22.71, 26.10, 29.32, 29.41, 29.59, 29.65, 29.68, 29.72, 30.35, 31.95, 52.05, 69.15, 73.46, 76.72, 77.04, 77.36, 107.98, 124.65, 142.38, 152.82, 166.91.

**Methyl 3,4,5-tris-pentadecyloxy-benzoate (1b)**
The procedure follows compound 1a. The product was afforded as white solid in 82% yield. m.p. 52 °C.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 0.88 (t, 9H, $J$=6.8 Hz), 1.30 (m, 6H), 1.49 (m, 6H), 1.8 (m, 6H), 3.89 (s, 3H), 4.01 (m, 6H), 7.25 (s, 2H)

$^{13}$C NMR (100 MHz, CDCl$_3$): 14.13, 22.71, 26.10, 29.32, 29.41, 29.59, 29.66, 29.70, 29.73, 30.35, 31.95, 52.10, 69.16, 73.49, 76.71, 77.03, 77.35, 107.97, 124.65, 142.36, 152.83, 166.95

3,4,5-tris-tridecyloxy-benzoic acid (2a)

A mixture of potassium hydroxide (0.52 g, 9.23 mmol), methyl 3,4,5-tris-alkyloxy benzoate (3.20 g, 2.89 mmol) and distilled water distilled water (2 ml), anhydrous ethanol (20 ml) were mixed and refluxed under stirring. After 2 hrs, TLC showed the reaction was complete. Then 50% HCl was added to acidify the solution to pH=1. The precipitate was filtered and dried in the vacuum oven at 50 °C for 1 day to give the product as a white solid in 95% yield. m.p. 64 °C.

3,4,5-tris-pentadecyloxy -benzoic acid (2b)

The procedure follows compound 2a. The product was afforded as white solid in 88% yield. m.p. 73 °C.

5,10,15,20-tetra[p-(3’,4’,5’-tris-tridecyloxybenzoyloxy)phenyl] porphyrin (3a)

A mixture of 3,4,5-tris-tridecyloxy-benzoic acid (1.00 g, 1.37 mmol), 5,10,15,20-tetra(p-hydroxy phenyl)porphyrin (0.19 g, 0.28 mmol), DCC( 0.28 g, 1.37 mmol), and DMAP
(0.17 g 1.37 mmol) in CH₂Cl₂ (15ml) and Et₂O (15ml) were stirred at room temperature for 48 hrs. After the reaction was complete, the mixture was extracted with methylene chloride and water. The organic layer was washed one time with 5% NaOH and brine, followed by twice with brine, dried over anhydrous magnesium sulfate and filtered. The solvent was evaporated. The residue was purified by flash chromatography using 3% ethyl acetate in hexane as eluent to afford the red solid product in 49% yield.

¹H NMR (400 MHz, CDCl₃): δ -2.78 (s, 2H), 0.89 (m, 36H), 1.37 (m, 216H), 1.56 (m, 24H), 1.91 (m, 24H), 4.15 (m, 24H), 7.60 (s, 8H), 7.63 (d, 8H, J = 8.4 Hz), 8.28 (d, 8H, J = 8.4 Hz), 8.95 (s, 8H)

¹³C NMR (100 MHz, CDCl₃): 14.15, 22.72, 26.13, 29.40, 29.47, 29.64, 29.70, 29.80, 30.42, 31.96, 69.78, 73.69, 108.73, 119.33, 120.18, 123.96, 131(b), 135.42, 139.63, 143.22, 151.06, 153.13, 165.25

IR: v (cm⁻¹) 1123.04, 1200.32, 1222.37, 1338.65, 1363.43, 1383.95, 1429.36, 1467.87, 1652.83, 1714.94, 2849.43, 2918.77

Anal. Calcd for C₂₂₈H₃₅₈N₄O₂₀: C, 78.80; H, 10.38; N, 1.61. Found: C, 78.67, H, 10.16, N, 1.51

Mass calcd for C₂₂₈H₃₅₈N₄O₂₀: 3472.7. MALDI Ms found: m/e 3472.7 (M+3).

5,10,15,20-tetrap(-3',4',5'-tris-pentadecyloxybenzoyloxy)phenyl] porphyrin (3b)

The procedure follows compound 3a and the product was afforded as red solid in 64% yield.
\( ^1 \text{H NMR (400 MHz, CDCl}_3 \): } \delta -2.78 (s, 2H), 0.89 (m, 36H), 1.37 (m, 264H), 1.56 (m, 24H), 1.91 (m, 24H), 4.15 (m, 24H), 7.60 (s, 8H), 7.63 (d, 8H, \( J = 8.4 \) Hz), 8.28 (d, 8H, \( J = 8.8 \) Hz), 8.95 (s, 8H)

\( ^{13} \text{C NMR (100 MHz, CDCl}_3 \): } 14.16, 22.74, 26.16, 26.20, 29.42, 29.50, 29.66, 29.73, 29.78, 29.82, 30.45, 31.98, 69.40, 73.71, 108.76, 119.36, 120.21, 123.99, 131(b), 135.45, 139.66, 143.25, 151.09, 153.15, 165.27

IR: \( \nu (\text{cm}^{-1}) \) 722.93, 751.29, 796.39, 1120.29, 1166.45, 1195.84, 1336.70, 1430.00, 1466.98, 1501.66, 1587.93, 1735.87, 2849.98, 2918.15

Anal. Calcd for C\(_{252}\)H\(_{406}\)N\(_4\)O\(_20\): C, 79.40; H, 10.74; N, 1.47. Found: C, 79.34, H, 10.74, N, 1.36

Mass Calcd for C\(_{252}\)H\(_{406}\)N\(_4\)O\(_20\): 3809.1. MALDI Ms found: m/e 3809.4 (M+3).

7.3 Experimental Details for Chapter 3

5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-4-iodo-decan-1-ol (4b)

A mixture of perfluorohexyl iodide (4.50 g, 10.00 mmol), 3-buten-1-ol (0.86g, 12.00 mmol) and fine copper powder (0.063 g, 1.00 mmol) was added into a sealed glass tube and heated to 120°C with rigorously stirring for 3 hrs. The reaction mixture was dissolved in diethyl ether and the solid was filtered off. The organic solution was dried over anhydrous magnesium sulfate. The solvent was evaporated under vacuum. The product was afforded as orange oil and used in the next step with out further purification.
Compounds 4a and 4c follow the same procedure as 4b.

11,11,12,12,13,13,13-heptafluoro-10-iodo-tridecan-1-ol (4d)

A solution of 9-decen-1-ol (0.70 g, 4.51 mmol) and 20 ml of hexane was added dropwise into the mixture of heptafluoro-1-iodopropane (2.00 g, 6.76 mmol) and tetrakis(triphenylphosphine)palladium(0) (0.21 g, 0.20 mmol) under ice-water bath. After 10 minutes the ice-water bath was removed and the mixture was stirred for 12 hrs. The solvent was evaporated and the residue was diluted with diethyl ether. The solid was filtered and solvent was extracted with water. The organic solution was dried over anhydrous magnesium sulfate. The solvent was evaporated under vacuum. The product was afforded as orange oil and used in the next step without further purification. NMR spectra have extra peaks and were not identified since the target compounds were not purified.

Compound 4e follows the same procedure as 4b.

4d: $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.55 (m, 12H), 1.94 (m, 2H), 2.77 (m, 2H), 3.67 (t, 2H, $J=6.6$ Hz), 4.37 (m, 1H)

4e: $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.55 (m, 12H), 1.94 (m, 2H), 2.77 (m, 2H), 3.65 (t, 2H, $J=6.6$ Hz), 4.33 (m, 1H)

5,5,6,6,7,7,8,8,9,9,10,10-tridecafluoro-decan-1-ol (5a)
A solution of 5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-4-iodo-decan-1-ol (5.28 g, 10.00 mmol) in 60 ml diethyl ether was added to a suspension of lithium aluminum hydride in 50ml anhydrous diethyl ether with ice-water bath under N\textsubscript{2}. After 10 minutes the ice-water bath was removed and the mixture was refluxed for 4 hrs. After the reaction was complete, 5 ml H\textsubscript{2}O was added into the mixture. The solids were filtered and washed with diethyl ether. The organic solvent was evaporated to afford orange oil and used in the next step without any further purification. NMR spectra have extra peaks and were not identified since the target compounds were not purified. \textsuperscript{97,98,99,100,101}

Compounds 5b-5e follow the same procedure as 5a.

\textbf{5d}: \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 1.35 (m, 14H), 1.59 (m, 2H), 2.04 (m, 2H), 3.65 (t, 2H, J=6.6 Hz)

\textbf{5e}: \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 1.35 (m, 14H), 1.59 (m, 2H), 2.01 (m, 2H), 3.64 (m, 2H)

\textbf{10-bromo-1,1-2,2-3,3-4,4-5,5-6,6-tridecafluoro-decane (6a)}

A mixture of 5,5,6,6,7,7,8,8,9,9,10,10,10-tridecafluoro-decan-1-ol (1.50 g, 3.70 mmol), cetyltrimethylammonium bromide (0.09 g, 0.25 mmol) and 48% HBr (8 ml) was refluxed under stirring for 8 hrs. The reaction mixture was cooled to room temperature and extracted with diethyl ether and water. The organic layer was washed three times with water, dried over anhydrous magnesium sulfate. The solvent was evaporated to afford
orange oil and used in the next step without further purification. NMR spectra have extra peaks and were not identified since the target compounds were not purified.97,102,103,101

Compounds 6b-6e follow the same procedure as 6a.

**6d:** $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.43 (m, 14H), 1.59 (m, 2H), 2.06 (m, 2H), 3.43 (t, 2H, $J$=6.8 Hz)

**6e:** $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.41 (m, 14H), 1.59 (m, 2H), 2.05 (m, 2H), 3.41 (t, 2H, $J$=6.8 Hz)

**Methyl 3,4,5-tris-(5,5-6,6-7,7-8,8-9,9-10,10,10-tridecafluoro-decyloxy)-benzoate (7a)**

A mixture of methyl 3,4,5-trihydroxybenoate (0.40 g, 2.15 mmol), 10-bromo-1,1,1-2,2-3,3-4,4-5,5-6,6-tridecafluoro-decane (3.90 g, 8.40 mmol) potassium carbonate (1.34 g, 9.70 mmol) were added in 25 ml DMF and heated to 80 °C under stirring for 48 hrs. The reaction mixture was extracted with methylene chloride and water. The organic layer was washed three times with brine, dried over anhydrous magnesium sulfate and evaporated. The residue was purified by flash chromatography using 10% ethyl acetate in hexane as eluent to afford the product as a white solid in 49% yield. m.p. 54 °C.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.89 (m, 12H), 2.17 (m, 6H), 3.90 (s, 3H), 4.02 (t, 2H, $J$=5.4 Hz), 4.07 (t, 4H, $J$=6 Hz), 7.28 (s, 2H)

$^{13}$C NMR (100 MHz, CDCl$_3$): 17.13, 17.27, 28.7, 29.7, 30.6, 52.2, 68.4, 72.6, 104-123, 108.0, 125.3, 141.8, 152.6, 166.6
Methyl 3,4,5-tris-(5,5-6,6-7,7-8,8-9,9-10,10,10-tridecafluoro-hexadecyloxy)-benzoate (7b)

The procedure follows compound 7a. The product was afforded as white solid in 50% yield. m.p. 64 °C.

$^1$H NMR (200 MHz, CDCl$_3$): $\delta$ 1.32 (m, 42H), 1.81 (m, 6H), 2.09 (m, 6H), 3.89 (s, 3H), 4.01 (m, 6H), 7.25 (s, 2H)

Methyl 3,4,5-tris-(5,5-6,6-7,7-8,8-9,9-10,10,-11,11,-12,12,12-heptadecafluoro-dodecyloxy)-benzoate (7c)

The procedure follows compound 7a. The product was afforded as white solid in 50% yield. m.p. 62.5 °C.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.86 (m, 12H), 2.17 (m, 6H), 3.89 (s, 3H), 4.05 (m, 6H), 7.24 (s, 2H)

$^{13}$C NMR (100 MHz, CDCl$_3$): 17.11, 17.32, 28.70, 29.69, 30.38, 30.60, 30.82, 52.21, 68.39, 72.64, 104-123, 108.01, 125.26, 141.80, 152.53, 166.63

Methyl 3,4,5-tris-(11,11,12,12,13,13,13-heptafluoro-tridecyloxy)-benzoate (7d)

The procedure follows compound 7a. The product was afforded as white solid in 55% yield. m.p. 25 °C.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.35 (m, 30H), 1.48 (m, 6H), 1.59 (m, 6H), 1.79 (m, 6H), 2.03 (m, 6H), 3.89 (s, 3H), 4.02 (m, 6H), 7.26 (s, 2H)
$\text{Methyl 3,4,5-tris-(11,11,12,12,13,13,14,14,14-nonafluorotetradecyloxy)-benzoate (7e)}$

The procedure follows compound $7a$. The product was afforded as white solid in 62% yield. m.p. 37 °C.

$^1\text{H NMR (400 MHz, CDCl}_3\text{:} \delta 1.31 \text{ (m, 30H)}, 1.48 \text{ (m, 6H)}, 1.59 \text{ (m, 6H)}, 1.79 \text{ (m, 6H)}, 2.03 \text{ (m, 6H)}, 3.89 \text{ (s, 3H)}, 4.01 \text{ (t, 6H)}, 7.251 \text{ (s, 2H)}$

$^{13}\text{C NMR (100 MHz, CDCl}_3\text{):} 20.08, 26.05, 29.11, 29.24, 29.29, 29.33, 29.41, 29.50, 29.60, 30.32, 30.54, 30.77, 30.99, 52.10, 69.11, 73.42, 104-123, 107.97, 124.72, 142.30, 152.81, 166.93$

$\text{3,4,5-tris-(5,5-6,6-7,7-8,8-9,9-10,10,10-tridecafluorodecyloxy)-benzoic acid (8a)}$

A mixture of potassium hydroxide (0.27 g, 4.70 mmol), methyl 3,4,5-tris-(5,5-6,6-7,7-8,8-9,9-10,10-tridecafluorodecyloxy)-benzoate (1.98 g, 1.50 mmol) distilled water (2 ml) and ethanol (20 ml) was refluxed under stirring. After 2 hrs, the TLC showed reaction was complete. Then 50% HCl was added to acidify the solution to pH=1. The precipitate was filtered and dried in the vacuum oven at 50 °C for one day to give the product as a white solid in 76.5 % yield. m.p. 78.5 °C.

Compounds $8d$ and $8e$ follow the same procedure as $8a$. 
5,10,15,20-tetra[p-(3’,4’,5’-tris-tridecafluorodecyloxybenzoyloxy)phenyl] porphyrin (9a)

A mixture of 3,4,5-tris-(5,5-6,6-7,7-8,8-9,9-10,10,10-tridecafluoro-decyloxy)-benzoic acid (0.91 g, 0.71 mmol), 5,10,15,20-tetra(p-hydroxy phenyl)porphyrin (0.10 g, 0.15 mmol), DCC (0.15 g, 0.71 mmol), and DMAP (0.19 g, 0.71mmol) in 15ml CH$_2$Cl$_2$ and 15 ml Et$_2$O was stirred at room temperature for 48 hrs. After the reaction was complete, the mixture was extracted with Et$_2$O and water. The organic layer was washed one time with 5% NaOH and, two times with brine, dried over anhydrous magnesium sulfate and filtered. The solvent was evaporated. The residue was purified by flash chromatography using 5% ethyl acetate in hexane as eluent. The obtained solid was then recrystallized with ether to give the product as a red dark solid in 21% yield.

$^1$H NMR (400 MHz,CDCl$_3$): $\delta$  -2.78 (s, 2H), 1.92 (m, 24H), 2.02 (m, 24H), 2.21 (m, 24H), 4.14 (t, 8H, $J = 5.4$ Hz), 4.22 (t, 16H, $J = 5.8$Hz), 7.63 (s, 8H), 7.65 (d, 8H, $J = 7.6$ Hz), 8.28 (d, 8H, $J = 8.4$ Hz), 8.94 (s, 8H)

$^{13}$C NMR (100 MHz, CDCl$_3$): 14.12, 17.22, 17.37, 22.66, 28.79, 29.77, 30.67, 31.60, 33.96, 68.62, 72.83, 100-130, 108.78, 119.29, 120.12, 124.56, 131, 135.43, 139.74, 142.66, 150.95, 152.84, 164.97

IR: $\nu$ (cm$^{-1}$) 530.57, 1144.56, 1222.62, 1363.46, 1432.72, 1714.99, 3004.63

Anal. Calcd for C$_{192}$H$_{130}$F$_{156}$N$_4$O$_{20}$: C, 39.92; H, 2.27; F, 51.30; N, 0.97. Found: C, 40.10, H, 2.09, N, 0.86.
5,10,15,20-tetra[p-(3’,4’,5’-tris-heptafluorotridecyloxybenzoyloxy)phenyl] porphyrin (9d)

The procedure follows compound 9a. The product was afforded as red solid in 54% yield.

$^1$H NMR (400 MHz, CDCl$_3$): δ -2.78 (s, 2H), 1.36 (m, 120H), 1.58 (m, 48H), 1.82 (m, 8H), 1.92 (m, 16H), 2.10 (m, 24H), 4.15 (m, 24H), 7.61 (s, 8H), 7.63 (d, 8H, $J = 8.4$ Hz), 8.28 (d, 8H, $J = 8.4$ Hz), 8.95 (s, 8H)

$^{13}$C NMR (100 MHz, CDCl$_3$): 20.08, 26.13, 29.13, 29.26, 29.31, 29.38, 29.44, 29.55, 29.65, 30.63, 69.34, 73.62, 100-130, 108.76, 119.32, 120.16, 124.02, 131, 135.42, 139.66, 143.20, 151.06, 153.12, 165.24

IR: ν (cm$^{-1}$) 727.17, 949.73, 1020.23, 1121.41, 1194.77, 1222.97, 1336.43, 1355.38, 1384.28, 1430.58, 1471.23, 1501.73, 1586.41, 1717.97, 1731.76, 2857.14, 2929.37

Anal. Calcd for C$_{228}$H$_{274}$F$_{84}$N$_4$O$_{20}$: C, 54.92; H, 5.54; F, 32.00; N, 1.12. Found: C, 55.05, H, 5.44, N, 1.07.

Mass calcd for C$_{228}$H$_{274}$F$_{84}$N$_4$O$_{20}$: 4983.9. MALDI Ms found: m/e 4983.4 (M+1).

5,10,15,20-tetra[p-(3’,4’,5’-trisnonafluorotetradecyloxybenzoyloxy)phenyl] porphyrin (9e)

The procedure follows compound 9a. The product was afforded as red solid in 61% yield.
$^1$H NMR (400 MHz, CDCl$_3$): δ -2.78 (s, 2H), 1.36 (m, 120H), 1.58 (m, 48H), 1.80 (m, 8H), 1.92 (m, 16H), 2.06 (m, 24H), 4.15 (m, 24H), 7.60 (s, 8H), 7.63 (d, 8H, $J = 8.4$ Hz), 8.28 (d, 8H, $J = 8.4$ Hz), 8.94 (s, 8H)

$^{13}$C NMR (100 MHz, CDCl$_3$): 20.10, 26.15, 29.14, 29.28, 29.34, 29.39, 29.46, 29.56, 29.67, 30.41, 30.57, 30.79, 31.02, 69.33, 73.63, 100-130, 108.74, 119.33, 120.17, 124.03, 131, 135.44, 139.67, 143.19, 151.06, 153.13, 165.25

IR: $\nu$ (cm$^{-1}$) 705.62, 738.93, 879.38, 1133.27, 1165.96, 1194.19, 1249.96, 1265.64, 1335.73, 1431.05, 1471.32, 1730.18, 2857.28, 2930.06

Anal. Calcd for C$_{240}$H$_{274}$F$_{108}$N$_4$O$_{20}$: C, 51.60; H, 4.94; N, 1.00. Found: C, 51.40, H, 4.82, N, 0.92

Mass calcd for C$_{240}$H$_{274}$F$_{108}$N$_4$O$_{20}$: 5583.9. MALDI Ms found: m/e 5583.5 (M+1).

7.4 Experimental Details for Chapter 5

5,10,15,20-tetra[p-(3’,4’,5’-tris-tridecyloxybenzoyloxy)phenyl] porphyrin zinc complex (10a)

A mixture of 5,10,15,20-tetra[p-(3’,4’,5’-tris-tridecyloxybenzoyloxyphenyl] porphyrin (0.10 g, 0.029 mmol), zinc acetate (0.026 g, 0.14 mmol) in 7.5 ml CH$_2$Cl$_2$ and 2.5 ml MeOH was stirred at room temperature for 8 hrs. After the reaction was complete, the reaction mixture was evaporated. The residue was purified by flash chromatography using 10% ethyl acetate in hexane as eluent to afford the product as pink solid in quantitative yield.
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 0.89 (m, 36H), 1.37 (m, 216H), 1.56 (m, 24H), 1.91 (m, 24H), 4.15 (m, 24H), 7.61 (s, 8H), 7.63 (d, 8H, $J = 8.4$ Hz), 8.28 (d, 8H, $J = 8.4$ Hz), 9.06 (s, 8H)

$^{13}$C NMR (100 MHz, CDCl$_3$): 14.15, 22.73, 26.13, 26.18, 29.41, 29.48, 29.64, 29.71, 29.75, 29.80, 30.43, 31.96, 69.38, 73.69, 108.73, 120.02, 120.34, 124.01, 132.21, 135.27, 140.28, 143.20, 150.35, 150.91, 153.12, 165.29

IR: $\nu$ (cm$^{-1}$) 1122.11, 1166.49, 1198.79, 1336.90, 1384.95, 1429.89, 1467.64, 1503.37, 1588.83, 1737.23, 2850.14, 2919.44, 3454.09

Anal. Calcd for C$_{228}$H$_{356}$N$_4$O$_{20}$Zn: C, 77.39; H, 10.14; N, 1.58. Found: C, 77.56, H, 10.40, N, 1.54

Mass calcd for C$_{228}$H$_{356}$N$_4$O$_{20}$Zn: 3534.6. MALDI Ms found: m/e 3534.8 (M+4).

$5,10,15,20$-tetra[$p$-(3’,4’,5’-tris-pentadecyloxybenzoyloxy)phenyl] porphyrin zinc complex (10b)

This compound follows the procedure of 10a. The product was afforded as pink solid in quantitative yield.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 0.87 (m, 36H), 1.28 (m, 264H), 1.56 (m, 24H), 1.89 (m, 24H), 4.15 (m, 24H), 7.61 (s, 8H), 7.63 (d, 8H, $J = 8.4$ Hz), 8.29 (d, 8H, $J = 8.4$ Hz), 9.06 (s, 8H)
$^{13}$C NMR (100 MHz, CDCl$_3$): 14.14, 22.71, 26.14, 26.18, 29.40, 29.48, 29.64, 29.70, 29.76, 29.80, 30.43, 31.95, 69.38, 73.69, 108.73, 120.02, 120.34, 124.01, 132.21, 135.26, 140.27, 143.20, 150.35, 150.91, 153.12, 165.28

IR: $\nu$ (cm$^{-1}$) 1121.97, 1165.96, 1197.21, 1336.31, 1387.85, 1429.67, 1467.68, 1502.93, 1735.76, 2849.14, 2917.07

Anal. Calcd for C$_{252}$H$_{404}$N$_4$O$_{20}$Zn: C, 78.10; H, 10.51; N, 1.45. Found: C, 77.99, H, 10.79, N, 1.44

Mass calcd for C$_{252}$H$_{404}$N$_4$O$_{20}$Zn: 3871.0. MALDI Ms found: m/e 3871.8 (M+4).

5,10,15,20-tetra[$p$-(3',4',5'-tris-heptafluorotridecyloxybenzoyloxy)phenyl] porphyrin zinc complex (10c)

This compound follows the procedure of 10a. The product was afforded as pink solid in quantitative yield.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.36 (m, 120H), 1.58 (m, 48H), 1.84 (m, 8H), 1.93 (m, 16H), 2.07 (m, 24H), 4.15 (m, 24H), 7.61 (s, 8H), 7.63 (d, 8H, $J = 8.4$ Hz), 8.29 (d, 8H, $J$ = 8.4 Hz), 9.05 (s, 8H)

$^{13}$C NMR (100 MHz, CDCl$_3$): 20.10, 26.13, 29.13, 29.26, 29.32, 29.38, 29.45, 29.55, 29.66, 30.40, 30.62, 30.85, 69.32, 73.62, 100-130, 108.73, 120.00, 120.32, 124.06, 132.19, 135.27, 140.30, 143.16, 150.34, 150.89, 153.11, 165.28

IR: $\nu$ (cm$^{-1}$) 1121.36, 1193.57, 1224.97, 1336.24, 1354.76, 1430.77, 1735.46, 2857.67, 2929.62
Anal. Calcd for C_{228}H_{272}F_{84}N_{4}O_{20}Zn: C, 54.23; H, 5.43; F, 31.60; N, 1.11. Found: C, 54.66, H, 5.51, N, 0.99.

Mass calcd for C_{228}H_{272}F_{84}N_{4}O_{20}Zn: 5045.83. MALDI Ms found: m/e 5045.0 (M+3).

5,10,15,20-tetra[p-(3',4',5'-tris-trisnonafluorotetradecyloxybenzoyloxy)phenyl] porphyrin zinc complex (10d)

This compound follows the procedure of 10a. The product was afforded as pink solid in quantitative yield.

^1H NMR (400 MHz,CDCl₃): δ 1.37 (m, 120H), 1.58 (m, 48H), 1.83 (m, 8H), 1.93 (m, 16H), 2.10 (m, 24H), 4.15 (m, 24H), 7.61 (s, 8H), 7.63 (d, 8H, J = 8.4 Hz), 8.29 (d, 8H, J = 8.4 Hz), 9.06 (s, 8H)

^13C NMR (100 MHz,CDCl₃): 20.10, 26.14, 29.13, 29.27, 29.33, 29.38, 29.45, 29.55, 29.66, 29.72, 30.41, 30.57, 30.79, 31.01, 69.32, 73.62, 100-130, 108.73, 120.00, 120.33, 124.06, 132.19, 135.27, 140.29, 143.16, 150.35, 150.90, 153.11, 165.27

IR: ν(cm⁻¹) 1132.83, 1165.26, 1192.83, 1221.70, 1335.06, 1429.94, 1470.67, 1499.29, 1731.94, 2856.03, 2926.60

Mass calcd for C_{240}H_{272}F_{108}N_{4}O_{20}Zn: 5645.8. MALDI Ms found: m/e 5645.5 (M+1).

5,10,15,20-tetra[p-(3',4',5'-tridecyloxybenzoyloxy)phenyl] porphyrin copper complex (11a)
A mixture of 5,10,15,20-tetra[p-(3’,4’,5’-tris-decyloxybenzoyloxyphenyl] porphyrin (0.10 g, 0.029 mmol), copper acetate monohydrate (0.029 g, 0.14 mmol) in 7.5 ml CH₂Cl₂ and 2.5 ml MeOH was stirred at room temperature for 8 hrs. After the reaction was complete, the solvent was evaporated. The residue was purified by flash chromatography using 10% ethyl acetate in hexane as eluent to afford the product as red solid in quantitative yield.

¹H NMR (400 MHz, CDCl₃): δ 0.87 (m, 36H), 1.28 (m, 216H), 1.54 (m, 24H), 1.88 (m, 24H), 4.10 (m, 24H), 7.51 (s, 8H) 

¹³C NMR (100 MHz, CDCl₃): 14.14, 22.72, 26.14, 29.36, 29.41, 29.43, 29.63, 29.69, 29.75, 29.79, 30.42, 31.97, 69.33, 73.64, 108.68, 119.85, 123.93, 143.19, 150.50, 153.10, 165.04

IR: ν (cm⁻¹) 1199.01, 1222.47, 1363.22, 1429.40, 1715.05, 2849.60, 2919.02, 3422.92

Anal. Calcd for C₂₂₈H₃₅₆CuN₄O₂₀: C, 77.43; H, 10.15; N, 1.58. Found: C, 77.23, H, 10.24, N, 1.55

Mass calcd for C₂₂₈H₃₅₆CuN₄O₂₀: 3533.6. MALDI Ms found: m/e 3533.8 (M+4).

5,10,15,20-tetra[p-(3’,4’,5’-tris-pentadecyloxybenzoyloxy)phenyl] porphyrin copper complex (11b)

This compound follows the procedure of 11a. The product was afforded as red solid in quantitative yield.
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 0.87 (m, 36H), 1.27 (m, 264H), 1.55 (m, 24H), 1.88 (m, 24H), 4.11 (m, 24H), 7.53 (s, 8H)

$^{13}$C NMR (100 MHz, CDCl$_3$): 14.12, 22.70, 22.72, 26.11, 26.15, 29.38, 29.41, 29.45, 29.62, 29.68, 29.74, 29.78, 30.40, 31.93, 31.96, 69.34, 73.66, 108.66, 119.3, 123.91, 143.17, 153.08, 165.03

IR: $\nu$ (cm$^{-1}$) 1001.35, 1121.00, 1165.65, 1336.89, 1430.66, 1500.57, 1737.40, 2850.16, 2918.18

Anal. Calcd for C$_{252}$H$_{404}$CuN$_4$O$_{20}$: C, 78.14; H, 10.51; N, 1.45. Found: C, 78.09, H, 10.78, N, 1.42

Mass calcd for C$_{252}$H$_{404}$CuN$_4$O$_{20}$: 3870.0. MALDI Ms found: m/e 3870.4 (M+3).

5,10,15,20-tetra[p-(3’,4’,5’-tris-heptafluorotridecyloxybenzoyloxy)phenyl] porphyrin copper complex (11c)

This compound follows the procedure of 11a. The product was afforded as red solid in quantitative yield. The product was afforded as red solid in quantitative yield.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.35 (m, 120H), 1.59 (m, 48H), 1.84 (m, 24H), 2.06 (m, 24H), 4.12 (m, 24H), 7.54 (s, 8H)

$^{13}$C NMR (100 MHz, CDCl$_3$): 20.07, 26.10, 29.11, 29.25, 26.36, 29.43, 29.53, 29.64, 30.38, 30.61, 30.84, 69.28, 73.59, 100-130, 108.66, 123.96, 143.12, 150.47, 153.06, 165.03
IR: $\nu$ (cm$^{-1}$) 725.64, 797.77, 908.50, 949.12, 1001.21, 1120.97, 1191.19, 1223.02, 1336.11,
1354.12, 1470.51, 1500.11, 1586.02, 1735.96, 2856.70, 2927.49

Anal. Calcd for C$_{228}$H$_{272}$CuF$_{84}$N$_4$O$_{20}$: C, 54.25; H, 5.43; N, 1.11. Found: C, 54.43, H,
5.28, N, 1.02

Mass calcd for C$_{228}$H$_{272}$CuF$_{84}$N$_4$O$_{20}$: 5044.8. MALDI Ms found: m/e 5044.7 (M+1).

5,10,15,20-tetra[p-(3’,4’,5’-tris-trisnonafluorotetradecyloxybenzoyloxy)phenyl]porphyrin copper complex (11d)

This compound follows the procedure of 11a. The product was afforded as red solid in
quantitative yield.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.34 (m, 120H), 1.59 (m, 48H), 1.88 (m, 24H), 2.07 (m,
24H), 4.12 (m, 24H), 7.54 (s, 8H)

$^{13}$C NMR (100 MHz, CDCl$_3$): 20.08, 26.10, 29.12, 29.25, 26.36, 29.44, 29.53, 29.64,
30.38, 30.55, 30.78, 31.00, 69.28, 73.59, 100-130, 108.65, 123.96, 143.12, 150.44,
153.06, 165.03

IR: $\nu$ (cm$^{-1}$) 735.25, 718.88, 797.85, 879.78, 1001.55, 1133.21, 1165.94, 1222.33, 1335.80,
1384.52, 1430.44, 1468.96, 1500.50, 1586.25, 1734.97, 2856.85, 2928.18

Anal. Calcd for C$_{240}$H$_{272}$CuF$_{108}$N$_4$O$_{20}$: C, 51.04; H, 4.85; N, 0.99. Found: C, 51.24, H,
4.64, N, 0.90

Mass calcd for C$_{240}$H$_{272}$CuF$_{108}$N$_4$O$_{20}$: 5644.8. MALDI Ms found: m/e 5044.5 (M+1).
5,10,15,20-tetra[p-(3’,4’,5’-tris-tridecyloxybenzoyloxy)phenyl]porphyrin magnesium complex (12a)

A mixture of 5,10,15,20-tetra[p-(3’,4’,5’-tris-tridecyloxybenzoyloxyphenyl)] porphyrin (0.10 g, 0.029 mmol), magnesium iodide (0.080 g, 0.29 mmol) in 8 ml CH₂Cl₂ and 0.06 ml triethylamine was stirred at room temperature for 8 hrs. After the reaction was complete, the reaction mixture was evaporated. The residue was purified by flash chromatography using 10% ethyl acetate in hexane as eluent to afford the product as green solid in 70% yield.

¹H NMR (400 MHz, CDCl₃): δ 0.88 (m, 36H), 1.29 (m, 216H), 1.55 (m, 24H), 1.89 (m, 24H), 4.13 (m, 24H), 7.58 (s, 8H), 7.59 (d, 8H, J = 6 Hz), 8.23 (d, 8H, J = 8.4 Hz), 8.96 (s, 8H)

¹³C NMR (100 MHz, CDCl₃): 14.15, 22.73, 26.13, 26.18, 29.41, 29.49, 29.65, 29.71, 29.76, 29.80, 30.42, 31.96, 69.36, 73.66, 108.71, 119.70, 120.75, 124.04, 132.06, 135.45, 141.18, 143.13, 150.07, 150.59, 153.06, 165.31

IR: v (cm⁻¹) 725.64, 797.77, 908.50, 949.12, 1001.21, 1120.97, 1191.19, 1223.02, 1336.11, 1354.12, 1470.51, 1500.11, 1586.02, 1735.96, 2856.70, 2927.49

Anal. Calcd for C₂₂₈H₃₅₆N₄O₂₀Mg: C, 78.30; H, 10.29; N, 1.60. Found: C, 78.05, H, 10.54, N, 1.82

Mass calcd for C₂₂₈H₃₅₆N₄O₂₀Mg: 3494.7. MALDI Ms found: m/e 3495.3 (M+1).
5,10,15,20-tetra[p-(3’,4’,5’-tris-pentadecyloxybenzoyloxy)phenyl]porphyrin magnesium complex (12b)

This compound follows the procedure of 12a. The product was afforded as green solid in 64% yield.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 0.87 (m, 36H), 1.29 (m, 264H), 1.53 (m, 24H), 1.87 (m, 24H), 4.11 (m, 24H), 7.55 (s, 8H), 7.56 (d, 8H, $J = 8$ Hz), 8.26 (d, 8H, $J = 8.4$ Hz), 8.94 (s, 8H)

$^{13}$C NMR (100 MHz, CDCl$_3$): 14.16, 22.73, 26.14, 26.19, 29.39, 29.42, 29.51, 29.66, 29.73, 29.78, 29.82, 30.42, 31.97, 69.35, 73.65, 108.68, 119.68, 120.72, 124.00 132.06, 135.45, 141.19, 143.09, 150.06, 150.53, 153.01, 165.31

IR: $\upsilon$(cm$^{-1}$) 722.28, 796.39, 861.30, 995.32, 1008.81, 1118.52, 1164.92, 1192.81, 1335.01, 1380.27, 1430.25, 1467.44, 1501.90, 1586.98, 1736.07, 2850.64, 2919.03

Anal. Calcd for C$_{252}$H$_{404}$N$_4$O$_{20}$Mg: C, 78.94; H, 10.62; N, 1.46. Found: C, 78.67, H, 10.44, N, 1.61

Mass calcd for C$_{252}$H$_{404}$N$_4$O$_{20}$Mg: 3831.1. MALDI Ms found: m/e 3832.0 (M+1).

5,10,15,20-tetra[p-(3’,4’,5’-tris-heptafluorotridecyloxybenzoyloxy)phenyl]porphyrin magnesium complex (12c)

This compound follows the procedure of 12a. The product was afforded as green solid in 77% yield.
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.38 (m, 120H), 1.54 (m, 48H), 1.79 (m, 8H), 1.85 (m, 16H), 2.07 (m, 24H), 4.08 (m, 24H), 7.52 (s, 8H), 7.55 (d, 8H, $J = 8$ Hz), 8.29 (d, 8H, $J = 8.4$ Hz), 8.95 (s, 8H)

$^{13}$C NMR (100 MHz, CDCl$_3$): 20.09, 26.13, 29.15, 29.29, 29.34, 29.41, 29.48, 29.57, 29.68, 30.39, 30.62, 30.84, 69.31, 73.55, 108.74, 109.13, 103-123, 119.66, 120.72, 124.02, 132.06, 135.47, 141.26, 143.05, 150.09, 150.52, 152.92, 165.29

IR: $\nu$ (cm$^{-1}$) 725.13, 796.28, 908.25, 948.88, 1120.79, 1193.12, 1223.32, 1335.79, 1385.78, 1430.72, 1470.90, 1501.44, 1587.08, 1629.60, 1736.37, 2856.88, 2927.91

Anal. Calcd for C$_{228}$H$_{272}$F$_{84}$N$_4$O$_{20}$Mg: C, 54.67; H, 5.47; N, 1.12. Found: C, 54.78, H, 5.43, N, 1.06.

Mass calcd for C$_{228}$H$_{272}$F$_{84}$N$_4$O$_{20}$Mg: 5005.9. MALDI Ms found: m/e 5007.8 (M+2).

5,10,15,20-tetra[p-(3',4',5'-tris-trisnonafluorotetradecyloxybenzoyloxy)phenyl]porphyrin magnesium complex (12d)

This compound follows the procedure of 12a. The product was afforded as green solid in 80% yield.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.38 (m, 120H), 1.62 (m, 48H), 1.81 (m, 8H), 1.89 (m, 16H), 2.06 (m, 24H), 4.11 (m, 24H), 7.55 (s, 8H), 7.56 (d, 8H), 8.26 (d, 8H, $J = 7.6$ Hz), 8.94 (s, 8H)
$^{13}$C NMR (100 MHz, CDCl$_3$): 20.10, 26.12, 26.15, 29.15, 29.30, 29.35, 29.41, 29.48, 29.58, 29.69, 30.40, 30.56, 30.78, 31.00, 69.30, 73.58, 108.69, 105-123(m), 119.66, 120.71, 124.04, 132.04, 135.46, 141.25, 143.06, 150.09, 150.52, 153.00, 165.30

IR: $\nu$ (cm$^{-1}$) 719.15, 797.29, 879.81, 1019.29, 1133.35, 1231.49, 1336.17, 1386.08, 1430.51, 1471.30, 1501.70, 1586.86, 1632.43, 1732.62, 2856.96, 2928.95

Anal. Calcd for C$_{240}$H$_{272}$F$_{108}$N$_4$O$_{20}$Mg: C, 51.39; H, 4.89; N, 1.00. Found: C, 51.46, H, 4.82, N, 0.93.

Mass calcd for C$_{240}$H$_{272}$F$_{108}$N$_4$O$_{20}$Mg: 5605.9. MALDI Ms found: m/e 5607.4 (M+2).

7.5 Experimental Details for Chapter 6

3,4,5-tris-(11-hydroxy-undecyloxy)-benzoic acid methyl ester (13a)

A mixture of methyl 3,4,5-trihydroxybezoate (1.48g, 8.06 mmol), 11-bromo-undecan-1-ol (8.10 g, 32.24 mmol) potassium carbonate (5.01g, 36.24 mmol) were added in 250 ml DMF and heated to 80 °C under stirring for 48 hrs. The reaction mixture was extracted with EtOAc and water. The organic layer was washed three times with brine, dried over anhydrous magnesium sulfate and evaporated. The residue was purified by flash chromatography using 50% ethyl acetate in hexane as eluent to afford the product as a white solid in 29% yield. m.p. 66 °C.

$^1$H NMR (400 MHz, CDCl$_3$): δ 1.28 (m, 42H), 1.46 (m, 6H), 1.55 (m, 6H), 1.80 (m, 6H), 3.62 (t, 6H $J$=6.4 Hz), 3.87 (s, 3H), 4.01 (m, 6H), 7.24 (s, 2H)
$^{13}$C NMR (100 MHz, CDCl$_3$): 25.77, 25.79, 26.08, 29.29, 29.37, 29.46, 29.49, 29.55, 29.60, 29.62, 29.68, 29.70, 30.32, 32.80, 52.14, 63.00, 69.14, 73.47, 107.96, 124.66, 142.31, 152.80, 166.98.

3,4,5-tris-(6-hydroxy-hexyloxy)-benzoic acid methyl ester (13b)

This compound follows the same procedure as 13a. The product was afforded as white solid in 30% yield.

$^1$H NMR (200 MHz, CDCl$_3$): $\delta$ 1.56 (m, 18H), 1.84 (m, 6H), 3.66 (m, 6H), 3.89 (s, 3H), 4.02 (m, 6H), 7.26 (s, 2H)

3,4,5-tris-(11-hydroxy-undecyloxy)-benzoic acid (14a)

A mixture of potassium hydroxide (0.30 g, 5.34 mmol), 3,4,5-tris-(11-hydroxy-undecyloxy)-benzoic acid methyl ester (1.16 g, 1.67 mmol) distilled water (10 ml), methanol (30 ml) was mixed and refluxed under stirring. After 5 hrs, the TLC showed reaction was complete. Then 3M HCl was added to acidify the mixture to pH=1. Then the precipitate was filtered, redissolved in ethyl acetate and washed with brine three times. The organic layer was dried over anhydrous sodium sulfate and evaporated to afford as a white solid in 92% yield. m.p. 73 $^\circ$C.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.30 (m, 42H), 1.47 (m, 6H), 1.55 (m, 6H), 1.80 (m, 6H), 3.64 (m, 6H), 4.04 (m, 6H), 7.30 (s, 2H)

3,4,5-tris-(6-hydroxy-hexyloxy)-benzoic acid (14b)
This compound follows the same procedure as 14a. The product was afforded as while solid in 95% yield.

$^1$H NMR (200 MHz, CDCl$_3$): $\delta$ 1.58 (m, 18H), 1.84 (m, 6H), 3.64 (m, 6H), 4.03 (m, 6H), 7.30 (s, 2H)

3,4,5-tris-[11-(tetrahydro-pyran-2-yloxy)-undecyloxy]-benzoic acid (15a)

A solution of 3,4,5-tris-(11-hydroxy-undecyloxy)-benzoic acid (0.5 g, 0.73 mmol), dihydro-pyran (DHP) (0.23 ml, 3.96 mmol) and catalytic amount of p-toluenesulfonic acid (p-TsOH) in anhydrous THF (10 ml) was stirred for 10 hrs at room temperature. The solid (excess p-TsOH) was filtered; the filtrate was evaporated and purified by flash chromatography using 30% ethyl acetate in hexane as eluent to afford the product as yellow oil in 79% yield.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.30 (m, 42H), 1.56 (m, 18H), 1.73 (m, 6H), 1.80 (m, 6H), 3.37 (m, 3H), 3.50 (m, 3H), 3.72 (m, 3H), 3.84 (m, 3H), 4.02 (m, 6H), 5.28 (m, 3H), 7.30 (s, 2H)

$^{13}$C NMR (100 MHz, CDCl$_3$): 19.70, 25.50, 26.03, 26.25, 26.28, 29.26, 29.34, 29.50, 29.55, 29.58, 29.66, 29.69, 29.74, 30.31, 30.77, 31.88, 62.30, 63.78, 67.71, 69.16, 73.50, 98.82, 108.52, 123.92, 142.96, 152.81, 170.85

3,4,5-tris-[6-(tetrahydro-pyran-2-yloxy)-hexyloxy]-benzoic acid (15b)
This compound follows the same procedure as 15a. The product was afforded as while solid in 51% yield.

\[ ^1H \text{ NMR (200 MHz, CDCl}_3\text{): } \delta 1.54 (m, 30H), 1.77 (m, 12H), 3.42 (m, 6H), 3.82 (m, 6H), 4.02 (m, 6H), 4.58 (m, 3H), 7.30 (s, 2H) \]


A mixture of 3,4,5-tris-[11-(tetrahydro-pyran-2-yloxy)-undecyloxy]-benzoic acid (0.3 g, 0.32 mmol), 5,10,15,20-tetra(p-hydroxy phenyl)porphyrin (0.043 g, 0.064 mmol), DCC (0.064 g, 0.3086 mmol), and DMAP (0.038 g, 0.31 mmol) in 15 ml CH\textsubscript{2}Cl\textsubscript{2} and 15 ml Et\textsubscript{2}O was stirred at room temperature for 48 hrs. After the reaction was complete, the mixture was extracted with methylene chloride and water. The organic layer was washed two times with brine, dried over anhydrous magnesium sulfate and filtered. The solvent was evaporated. The residue was purified by flash chromatography using 30% ethyl acetate in hexane as eluent to afford the product as red solid in 75% yield. m.p. 69 °C.

\[ ^1H \text{ NMR (200 MHz, CDCl}_3\text{): } \delta -2.78 (s, 2H), 1.30 (m, 240H), 1.82 (m, 48H), 3.41 (m, 24H), 3.76 (m, 24H), 4.13 (m, 24H), 4.58 (m, 12H), 7.60 (s, 8H), 7.66 (d, 8H \ J = 8 Hz), 8.30 (d, 8H) \]

This compound follows the same procedure as 16a. The product was afforded as red solid in 74% yield. m.p. 93 °C.

\(^1\)H NMR (200 MHz, CDCl\(_3\)): \(\delta\) -2.78 (s, 2H), 1.57 (m, 120H), 1.89 (m, 48H), 3.45 (m, 24H), 3.84 (m, 24H), 4.16 (m, 24H), 4.60 (m, 12H), 7.59 (s, 8H), 7.62 (d, 8H \(J = 8.6\) Hz), 8.27 (d, 8H \(J = 8.2\) Hz), 8.95 (s, 8H)

5,10,15,20-tetra\(-p\)-(3',4',5'-tris-hydroxy-undecyloxy)phenyl| porphyrin (17a)

5,10,15,20-tetra\(-p\)-(3',4',5'-tris- tetrahydro-pyran-2-yloxy-undecyloxy)phenyl|porphyrin (0.2 g, 0.046mmol) in methanol with catalyst amount p-TsOH (p-toluenesulfonic acid) was refluxed for 6 hrs. The mixture turned green after the addition. After reaction was complete, the solvent was evaporated. The residue was purified by flash chromatography using 30% ethyl acetate 50% hexane and 20% methanol as eluent to afford the product as red solid in 74% yield.

\(^1\)H NMR (200 MHz, CDCl\(_3\)): \(\delta\) -2.78 (s, 2H), 1.34 (m, 192H), 1.87 (m, 24H), 3.65 (m, 24H), 4.16 (m, 24H), 7.60 (s, 8H), 7.66 (d, 8H), 8.28 (d, 8H \(J = 7.8\) Hz), 8.96 (s, 8H)

5,10,15,20-tetra\(-p\)-(3',4',5'-tris-hydroxy-hexyloxy)phenyl| porphyrin (17b)

This compound follows the same procedure as 17a. The product was afforded as red solid in 69% yield.

\(^1\)H NMR(200 MHz,CDCl\(_3\)): \(\delta\) -2.78 (s,2H), 1.56 (m, 72H), 1.90 (m, 24H), 3.67 (m, 24H), 4.14 (m, 24H), 7.60 (s, 8H), 7.65 (d, 8H), 8.27 (d, 8H \(J = 8\) Hz), 8.95 (s, 8H)
A mixture of 5,10,15,20-tetra[3’,4’,5’-tris-hydroxyl-undecyloxy]phenyl porphyrin (0.4 g, 0.13 mmol), (S)-(−)-2-methylbutyric acid (0.25 g, 2.5 mmol), DCC (0.51 g, 2.46 mmol), and DMAP (0.3 g, 2.46 mmol) in 20 ml CH₂Cl₂ and 20 ml Et₂O was stirred at room temperature for 48 hrs. After the reaction was finished, the mixture was poured into methylene chloride and extracted with 1M NaOH once and twice with brine. The organic layer was dried with anhydrous sodium sulfate and the solvent was evaporated. The crude compound was purified by flash chromatography using 30% ethyl acetate in 70% hexane as eluent to afford the product as red solid in 72% yield.

**18a**

\[^1\text{H} \text{NMR (400 MHz, CDCl}\_3): \delta -2.76 (s, 2H), 0.90 (m, 48H), 1.16 (m, 48H), 1.33 (m, 144H), 1.54 (m, 24H), 1.66 (m, 48H), 1.91 (m, 24H), 2.37 (m, 12H), 4.08 (m, 24H), 4.16 (m, 24H), 7.61 (s, 8H), 7.64 (d, 8H, \text{J}=8.4 \text{Hz}), 8.29 (d, 8H, \text{J}=8.4 \text{Hz}), 8.96 (s, 8H)\]

\[^{13}\text{C} \text{NMR (100 MHz, CDCl}\_3): 11.66, 16.68, 25.97, 26.16, 26.83, 28.72, 29.30, 29.34, 29.40, 29.46, 29.58, 29.64, 29.74, 30.42, 41.16, 64.30, 69.37, 73.67, 108.76, 119.33, 120.18, 123.99, 135.44, 139.64, 143.21, 151.06, 153.12, 165.25, 176.87\]

IR: \(\nu(\text{cm}^{-1})\) 730.28, 750.19, 796.01, 1020.02, 1122.32, 1152.73, 1193.17, 1335.65, 1384.51, 1429.99, 1464.04, 1501.40, 1585.86, 1733.73, 2854.52, 2928.01

**18b**

This compound follows the same procedure as **18a**. The product was afforded as red solid in 74% yield.
Methyl 3,4,5-tris-(3-hydroxy-2-methyl-propoxy)-benzoate (19)

Methyl-3,4,5-trihydroxybenzoate (0.65 g, 3.49 mmol) was dissolved in dry acetone (40 ml) in a 100 ml round-bottom flask equipped with a stirbar. To this solution was then added K₂CO₃ (3.61 g, 26.14 mmol). The resulting mixture was heated to 60°C and stirred vigorously for 0.5 hr. (R)-(−)-3-Bromo-2-methyl-1-propanol (1.92 g, 12.55 mmol) was dissolved in 10 ml acetone and added slowly to the mixture. Then the reaction mixture was refluxed for 18 hr. After the reaction was completed, the solvent was evaporated and the residue was extracted with methyl chloride and brine. The organic layer was dried over anhydrous sodium sulfate and the solvent was evaporated under reduced pressure. The crude compound was purified by flash chromatography using 30% ethyl acetate in 70% hexane as eluent to afford the product in 27% yield.

1H NMR (400 MHz, CDCl₃): 0.97 (d, 3H, J=6.8 Hz), 1.04 (d, 6H, J=6.8 Hz), 2.24 (m, 3H), 3.71 (m, 6H), 3.89 (s, 3H), 4.05 (m, 6H), 7.29 (s, 2H)
$^{13}$C NMR (50 MHz, CDCl$_3$): 13.43, 13.66, 35.70, 36.05, 52.22, 65.92, 66.02, 72.46, 107.75, 125.30, 141.18, 152.08, 166.48

3,4,5-tris-(3-hydroxy-2-methyl-propoxy)-benzoic acid (20)

A mixture of potassium hydroxide (0.15 g, 2.64 mmol), methyl 3,4,5-tris-(3-hydroxy-2-methyl-propoxy)-benzoate (0.33 g, 0.82 mmol), distilled water (10 ml) and methanol (30 ml) was mixed and refluxed under stirring. After 5 hrs, the TLC showed the reaction was complete. Then 3M HCl was added to acidify the mixture to pH=1. The solid filtered was dissolved in ethyl acetate and washed with brine three times. The organic layer was dried over anhydrous sodium sulfate and the solvent was evaporated to afford the product as a white solid in 97% yield.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 0.99 (d, 3H, $J$=7.2Hz), 1.05 (d, 6H, $J$=6.8Hz), 2.26 (m, 3H), 3.72 (m, 6H), 4.11 (m, 6H), 7.30 (s, 2H)

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A solution of 3,4,5-tris-(3-hydroxy-2-methyl-propoxy)-benzoic acid (0.3 g, 0.78 mmol), DHP (0.26 ml, 4.19 mmol) and catalytic amount of p-TsOH in anhydrous THF (10 ml) was stirred for 10 hrs at room temperature. The solid (p-TsOH) was filtered. The filtrate was evaporated and purified by flash chromatography using 50% ethyl acetate in hexane as eluent to afford the product as yellow oil in 46% yield. m.p. 143 °C.
1H NMR (200 MHz, CDCl3): δ 1.10 (d, 9H, $J$=6 Hz), 1.53 (m, 18H), 2.29 (m, 3H), 3.43 (m, 6H), 3.79 (m, 12H), 4.58 (m, 3H), 7.33 (s, 2H)

A mixture of benzoic acid 21 (0.18 g, 0.28 mmol), 5,10,15,20-tetra(p-hydroxyphenyl)porphyrin (0.037 g, 0.054 mmol), DCC (0.056 g, 0.27 mmol), and DMAP (0.033 g, 0.27 mmol) in 15 ml CH2Cl2 and 15 ml Et2O was stirred at room temperature for 48 hrs. After the reaction was complete, the mixture was extracted with methylene chloride. The organic layer was washed two times with brine, dried over anhydrous magnesium sulfate and filtered. The solvent was evaporated. The residue was purified by flash chromatography using 30% ethyl acetate in hexane as eluent to afford the product in 54% yield.

1H NMR (200 MHz, CDCl3): δ –2.78 (s, 2H), 1.17 (d, 36H, $J$=6.6 Hz), 1.58 (m, 72H), 2.48 (m, 12H), 3.52 (m, 24H), 3.83 (m, 24H), 4.10 (m, 24H), 4.64 (m, 12H), 7.62 (s, 8H), 7.66 (d, 8H, $J$=8.4 Hz), 8.28 (d, 8H, $J$=8.2 Hz), 8.95 (s, 8H)

A mixture of THP protected porphyrin 22 (0.2 g, 0.046 mmol) in methanol with catalyst amount p-TsOH (p-toluenesulfonic acid) was refluxed for 18hrs. The mixture turned green when reaction started. After the reaction was complete, the solvent was evaporated. The residue was purified by flash chromatography using 60% ethyl acetate 20% hexane and 20% methanol as eluent to afford the product as red solid in 50% yield.
$^1$H NMR (200 MHz, CDCl$_3$): $\delta$ −2.78 (s, 2H), 1.13 (m, 36H), 2.33 (m, 12H), 3.80 (m, 24H), 4.20 (m, 24H), 7.62 (d, 8H, $J$= 7.8 Hz), 7.65 (s, 8H), 8.30 (d, 8H, $J$= 7.8 Hz), 8.94 (s, 8H)

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A mixture of porphyrin 23 (0.04 g, 0.019 mmol), dodecanoic acid (0.089 g, 0.44 mmol), DCC (0.092 g, 0.44 mmol), and DMAP (0.054 g, 0.44 mmol) in 10 ml CH$_2$Cl$_2$ and 10 ml Et$_2$O was stirred at room temperature for 48 hrs. After the reaction was finished, the mixture was extracted twice with methylene chloride and brine. The organic layer was dried with anhydrous sodium sulfate and the solvent was evaporated. The crude compound was purified by flash chromatography using 20% ethyl acetate hexane as eluent to afford the product as red solid in 70% yield.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ −2.75 (s, 2H), 0.83 (m, 36H), 1.18 (m, 228H), 1.66 (m, 24H), 2.34 (m, 24H), 2.45 (m, 12H), 4.19 (m, 48H), 7.62 (s, 8H), 7.64 (d, 8H, $J$= 8.8 Hz), 8.30 (d, 8H, $J$= 8.4 Hz), 8.96 (s, 8H)

$^{13}$C NMR (100 MHz, CDCl$_3$): 14.04, 14.11, 14.14, 14.18, 22.67, 22.71, 25.06, 29.23, 29.26, 29.33, 29.37, 29.50, 29.54, 29.62, 29.63, 31.90, 31.94, 33.34, 34.23, 34.35, 65.67, 66.14, 70.90, 75.30, 76.72, 108.70, 119.30, 120.15, 124.29, 135.44, 139.72, 142.88, 150.99, 152.81, 164.99, 173.83, 173.87

IR: $\nu$(cm$^{-1}$) 737.54, 798.35, 861.43, 939.29, 1019.49, 1120.79, 1166.55, 1195.06, 1337.29, 1392.17, 1430.82, 1467.22, 1502.48, 1589.06, 1635.50, 1734.58, 2850.48, 2919.29
3,4,5-tris-(3-hydroxy-2-methyl-propoxy)-benzoic acid (20) (0.11 g, 0.29 mmol) was dissolved in anhydrous DMF under N₂ in a 50 ml round-bottom flask. Sodium hydride (0.068 g, 2.85 mmol) was added slowly into the solution at 0 °C. The mixture was stirred at room temperature under the protection of N₂ for 1 hr. Then 1-bromo-tridecane (0.75 g, 2.85 mmol) was added to the solution. After 20 hrs, the reaction was completed. DMF was evaporated under reduced pressure by oil pump. The crude compound was extracted with Et₂O and washed with brine for three times. The organic layer was dried with anhydrous sodium sulfate and the solvent was evaporated. The crude compound was purified by flash chromatography using 20% ethyl acetate in hexane as eluent to afford the product as clear oil in 18% yield.

$^1$H NMR (400 MHz, CDCl₃): δ 0.88 (m, 9H), 1.09 (dd, 9H), 1.25 (m, 60H), 1.56 (m, 6H), 2.25 (m, 3H), 3.43 (m, 12H), 3.99 (m, 6H), 7.33 (s, 2H)

$^{13}$C NMR (100 MHz, CDCl₃): 14.13, 14.41, 22.70, 26.20, 29.38, 29.53, 29.69, 29.77, 31.94, 34.16, 35.07, 71.17, 71.32, 71.41, 72.74, 73.26, 75.87, 76.71, 108.29, 123.78, 142.84, 152.72, 171.29

A mixture of 25 (0.12 g, 0.13 mmol), 5,10,15,20-tetra(p-hydroxy phenyl)porphyrin (0.017 g, 0.026 mmol), DCC (0.027 g, 0.13 mmol), and DMAP (0.016 g, 0.13 mmol) in 10 ml CH₂Cl₂ and 10 ml Et₂O was stirred at room temperature for 48 hrs. After the reaction was finished, the mixture was extracted with methylene chloride and washed
with brine twice. The organic layer was dried with anhydrous sodium sulfate and the solvent was evaporated. The crude residue was purified by flash chromatography using 10% ethyl acetate hexane as eluent to afford the product as red sticky oil in 78% yield.

$^1$H NMR (200 MHz, CDCl$_3$): δ –2.78 (s, 2H), 0.89 (m, 36H), 1.23 (m, 276H), 1.58 (m, 24H), 2.31 (m, 12H), 3.44 (m, 48H), 4.11 (m, 24H), 7.61 (s, 8H), 6.77 (d, 8H $J$=9.8 Hz), 8.27 (d, 8H $J$=8.2Hz), 8.95 (s, 8H)

$^{13}$C NMR (75 MHz, CDCl$_3$): 14.06, 14.09, 14.47, 22.64, 22.68, 24.68, 25.46, 26.23, 29.33, 29.37, 29.53, 29.65, 29.68, 29.81, 31.89, 31.92, 34.27, 34.92, 35.16, 55.74, 71.36, 71.44, 72.77, 73.30, 76.01, 108.55, 119.32, 120.14, 124.01, 135.39, 139.63, 143.05, 151.07, 152.99, 165.12

IR: $\nu$ (cm$^{-1}$) 754.56, 800.58, 861.49, 950.92, 1017.80, 1115.45, 1165.36, 1191.00, 1335.37, 1430.28, 1466.31, 1501.42, 1588.31, 1736.61, 2853.19, 2924.06
Chapter 8

Conclusion

Four classes of target compounds were synthesized and identified by $^1$H NMR, $^{13}$C NMR, IR, Mass Spectroscopy and elemental analysis. Their chemical structures are listed as follows.

1. Nonfluorinated porphyrins

3a. $R=\text{C}_{13}\text{H}_{27}$
3b. $R=\text{C}_{15}\text{H}_{31}$
2. Fluorinated porphyrins

9a. $R=C_6F_{13}$  $n=4$
9d. $R=C_3F_7$  $n=10$
9e. $R=C_4F_9$  $n=10$
3. Metalloporphyrins

10a. R=C_{13}H_{27}
10b. R=C_{15}H_{31}
10c. R=C_{10}H_{22}C_{3}F_{7}
10d. R=C_{10}H_{22}C_{4}F_{9}

11a. R=C_{13}H_{27}
11b. R=C_{15}H_{31}
11c. R=C_{10}H_{22}C_{3}F_{7}
11d. R=C_{10}H_{22}C_{4}F_{9}
4. Chiral porphyrins
24: $R = C_{11}H_{23}$

26: $R = C_{13}H_{27}$
The target nonfluorinated porphyrins were synthesized and exhibit the phase sequence of $\text{Iso} \rightarrow \text{Col}_h \rightarrow \text{Col}_{ho} \rightarrow \text{Cr}$. The optical studies have shown that the nonfluorinated porphyrins are highly absorptive and fluorescent. Spontaneous homeotropic alignment was obtained and the factors were investigated. The blend 1 composed of pure porphyrin 3b and PCBM was studied by POM, DSC, UV-vis spectra, fluorescence emission and synchrotron X-ray diffraction. The fluorescence was quenched upon the addition of PCBM suggesting electron transfer in the mixture. Highly ordered nanostructured thin films of blend 1 were prepared by simple thermal annealing. The nature of their homeotropic alignment is well confirmed. The concept demonstration provides new insight on fabricating defect free large area bulk heterojunction thin films with directed molecular arrangement.

In order to improve the homeotropic alignment, fluorinated porphyrins were synthesized. They exhibit the phase sequence of $\text{Iso} \rightarrow \text{Col}_h \rightarrow \text{Col}_{ho}/\text{Cr}$. With the fluorine atoms on the alkyl chains, a much better homeotropic alignment with an almost completely black area was achieved which is a big improvement in enhancing the alignment. For the first time, defect-free hexagonal lattice fluorinated porphyrin thin films were fabricated and well characterized. This ability to self-assemble large $\pi$-conjugated discotic molecules into highly ordered nanostructures holds great promise for high performance PV devices.

The intermediate fluorinated benzoic acids also have the surprising property that they exhibit hexagonal LC phase by hydrogen bonding, on top of which, cubic phase was observed at the optical isotropic temperature by small-angle X-ray diffraction.
New mesophases of the nonfluorinated complexes were induced by the metal insertion into the porphyrin ring and the phase sequence can be summarized as \textbf{Iso}→\textbf{P}→\textbf{Cr}. The fluorinated complexes have the phase sequence of: \textbf{Iso}→\textbf{Col}_h→\textbf{Col}_{ho}→\textbf{Cr}. All the mesophases need X-ray confirmation. Zinc and copper complexes have strong absorption at UV-vis spectra while the magnesium complexes have weak absorbance. Strong fluorescence emission was obtained for metal free porphyrins, zinc and magnesium complexes and was almost completely quenched for copper complexes. Thin films of UV-Vis spectra were studied.

Fluorinated copper complexes show strong tendency toward homeotropic alignment exceptionally from other metal complexes. They might be good candidates for PV materials.

To study the application in devices, heterojunction solar cells were studied by Dr. Dai’s group. Preliminary results show that with the treatment of annealing, the bilayer-heterojunction cell has the power conversion efficiencies (PCEs) of 0.528%. Though the efficiency is not high enough, it is promising to obtain better performance by optimizing the homeotropic alignment and the weight ratio of porphyrin and PCBM. Further investigation on the device performance for fluorinated porphyrins is under the way.

Three kinds of chiral porphyrins for optical applications were successfully synthesized. Two of them seem to have LC phase but further identifications need to be done by X-ray diffraction. The optical properties are similar to the previous synthesized porphyrins. Further characterization of the phase behavior is needed for their relevance in device application.
References


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