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Synthesis of bowlic liquid crystals containing a cyclotrimeratrylene core

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SYNTHESIS OF BOWLIC LIQUID CRYSTALS
CONTAINING A CYCLOTRIVERATRYLENE CORE

A Thesis

Presented to

The Faculty of the Department of Chemistry

San Jose State University

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

Lanchi Phuoc Vo

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ABSTRACT

SYNTHESIS OF BOWLIC LIQUID CRYSTALS CONTAINING A CYCLOTRIVERATRYLENE CORE

by Lanchi P. Vo

Some hexaesters derived from cyclotrimeratrylene (CTV) exhibit liquid crystalline phases, in which the bowl-shape molecules stack in parallel columns. This semi-ordered arrangement could give rise to interesting electro-optical properties. To study their liquid crystalline (mesomorphic) behavior, a series of eight compounds with mono- or dialkyloxy substituted benzoate side chains (-R) were synthesized and characterized. Two of these compounds also contain cyano-terminated side chains prepared to potentially facilitate molecular alignment in an electric field.

CTV

(R = OCH₃)

Optical microscopy reveals the presence of mesophases for hexaesters with para-alkyloxy substituted benzoate side chains [R = -OC(O)-C₆H₄-O-C_nH_{2n+1}, n = 8, 8 & 10, 10, 12]. The mesophase of the hexa(3,4-dioctyloxybenzoate) ester can only be observed upon cooling the sample from its isotropic temperature (monotropic). Compounds with 3,5-dialkyloxy and/or cyano-substituted side chains do not exhibit liquid crystalline phases.

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INTRODUCTION

Several classes of organic compounds exist in a liquid crystalline phase. In this state, the molecules maintain ordered arrangement in one or more dimensions but also exhibit some degree of disorder in the other dimension(s). In general, a liquid crystal molecule must possess a rigid segment (such as rod or disc shape) which induces the orientational order, and in most cases, some amorphous segment (usually in the form of flexible alkyl chain) which inhibits completed crystallization of the molecule.¹

Organic molecules that exhibit the liquid crystalline phase (also called the mesophase) within certain temperature ranges are called thermotropic liquid crystals. More than one mesophase can be formed by each type of liquid crystal, depending on the temperature range or other external conditions.¹ Common types of thermotropic liquid crystals are the rod-like calamitics, the chiral cholesterics, the disc-like discotics, and the cone-shaped bowlics or pyramidics.³ Representative structures and the possible alignments of these liquid crystals are illustrated in Figure 1.^{1, 4, 5}

The relative fluidity of the mesophase coupled with the dipole moment of some liquid crystals allows for the alignment and/or switching of the bulk orientation under the influence of temperature, electromagnetic field, or mechanical forces. Many interesting applications are derived from these unique properties. Familiar applications include the display industries, which use nematic or twisted nematic liquid crystals in their flat panel monitors, automobile dash-boards, electronic calculators, watches and household appliances.⁶ The changing color of cholesteric liquid crystals in response to changes in temperature or electric field is utilized in color-indicator thermometers, sensors and other display applications.⁷

Calamitic Structures

Nematic

Smectic A

Smectic C

Twisted Nematic (cholesteric)

Figure 1. Thermotropic liquid crystals and common mesophases.

Discotic and Bowlic Structures

Hexagonal Columnar Structures

Figure 1. Cont.

Discotic and bowlic liquid crystals are the more recent development. Like the discotics, the mesophases of bowlic liquid crystals can be tubular or hexagonal columnar.² Because of the cone-shaped core, bowlic liquid crystals possess a net dipole moment along their axis. In addition, the columns formed by the stacked bowlic structure are more stable than the flat discotic stackings.^{8,13} Bowlic liquid crystals can thus be arranged and frozen into ferroelectric/anti-ferroelectric layers^{8,9} or strong superconductor wires.⁴ The cavity formed by those pyramidal mesogens can also be used as complexing agents for organic molecules.^{10,11}

Bowlic mesogens consist of the hexa-substituted cyclotricatechylene^{3,13} or macrocyclic polyamines,¹⁷ the octa-substituted cyclotetracatechylene,¹⁸ and the larger metacyclophane core with twelve side chains.^{9,19} Common bowlic mesogens are illustrated in Figure 2.

Figure 2. Representative bowlic mesogens.

The mesogenic behaviors of bowlic liquid crystals based on cyclotrimeratrylene core (CTV) were reported by Zimmermann et al.,^{3, 15} J. Malthete et al.,^{8, 13, 16} and most recently, by Jalik et al.¹⁴ A series of hexa-substituted CTV compounds from literature are listed in Figure 3. Several of those molecules were reported to form mesophases when the side chains are of sufficient length.^{3, 8, 15, 16}

Figure 3. Known hexaethers and hexaesters with cyclotricatechylene core.

To achieve useful anisotropic properties, the liquid crystal columns must be aligned in parallel stacks with all the cones oriented in a regular fashion. The vertical stacking of such molecules on a polar substrate (such as glass) may be facilitated with a polar anchoring agent (e.g. $R = \text{---}(\text{CH}_2)_n\text{---COOH}$). The polar substituents would anchor themselves onto the substrate, serving as templates for subsequent stacking. The use of octadecyltriethoxysilane treated substrate to align chiral CTV based liquid crystals has been reported.¹⁴

At high temperature (~ 200 °C), the CTV cone was reported to undergo a conformational inversion.⁸ This behavior could be used to polarize the columns into ferroelectric arrangement under the directional influences of external forces at the inversion temperature.

To further investigate the electro-optical properties of this mesogenic core, a series of CTV based liquid crystals were synthesized. The length and branching pattern of the alkyl side chains were varied to investigate their effect on the mesogenic properties. To facilitate the electro-optical switching behavior critical for the alignment process, cyano groups (-CN), which possess strong dipole moment, were also incorporated into the side chains of some CTV based molecules.

RESULTS AND DISCUSSION

Synthetic Strategy

A series of hexa-substituted cyclotricatechylenes were synthesized based on a general procedure outlined in Scheme 1. CTV was obtained from the condensation of veratrole and formaldehyde.^{22, 23} After demethylation with boron tribromide,²³ the resulting cyclotri-catechylene (CTC) was acylated with the appropriate acylchloride to form the desired products.¹³

Since compound **1c** (Fig. 3) has the widest mesomorphic temperature range (< 20 °C to 188 °C),^{13, 16} a homologous series of different aliphatic chain lengths based on this structure were synthesized. X-ray diffraction studies showed that the columnar phase of **1c** assumes a slight helical twist due to the unsymmetrical arrangement of the paraffinic side chains.¹⁶ The loosely interlocking arrangement of the helices among otherwise independent columns imparts a quasi-crystalline state to the columnar phase.¹⁶ To study the

effects of peripheral configuration on the mesomorphic properties, the 3,4- and 3,5-dialkyloxy substituted benzoate side chains were also incorporated into the CTV core.

Scheme 1. Synthetic Procedure for Hexaesters of Cyclotricatechylene

In addition, novel CTV based compounds with cyano terminated side chains and a hexaester with mixed chain lengths were synthesized. Attempts to synthesize a hexaacid anchoring agent ($R = -CH_2-COOH$) were unsuccessful. Figure 4 summarizes the synthetic scope of this study.

Bowlic core

CTV: $R = -CH_3$

CTC: $R = -H$

Hexaesters

- 1a:** $n = 7$; $X = CH_3$
- 1b:** $n = 9$; $X = CH_3$
- 1c:** $n = 11$; $X = CH_3$
- 1d:** $n = 7 \text{ \& } 9$; $X = CH_3$
- 1e:** $n = 6$; $X = CN$

- 2a:** $n = 7$; $X = CH_3$
- 2b:** $n = 6$; $X = CN$

- 3:** $n = 7$; $X = CH_3$

Figure 4. Synthetic scope for CTV based liquid crystals.

The general synthetic scheme consists of assembling the CTV core and the side chains independently, then coupling them with a final esterification.

Central Core

Synthesis of Cyclotrivenatrylene (CTV)

Preparation of the CTV precursor was carried out under the conditions published by Robinson in 1915.²² Other selected procedures were reviewed elsewhere.²⁵ Under acidic condition, veratrole reacts with formaldehyde to form the veratryl cations, which trimerize to yield CTV. Possible side products from this reaction, therefore, are likely to be higher cyclic oligomers.²⁵ A general mechanism of this reaction is illustrated in Scheme 2.

Toward the end of the addition, the mixture thickens. At this stage, it is important to maintain the reaction temperature and vigorous stirring to minimize the formation of dark purple side products. Large excess of formaldehyde solution could be expected to improve the agitation. Because of the highly acidic mixture, filtration and washing should be carried out with a fritted glass funnel.

The simple ¹H-NMR spectrum of the product (Figure 5) confirms the symmetrical cyclic trimeric structure.^{23, 24} Partially due to the steric compression, the pseudo-axial hydrogens of the methylene bridges resonate further downfield from the pseudo-equatorial hydrogens.^{13, 25}

Synthesis of Cyclotricatechylene (CTC)

Demethylation of CTV by boron tribromide occurs readily at room temperature in methylene chloride.^{10, 23} The completion of the demethylation is evident by the disappearance of the methyl signal in the ¹H-NMR. Comparable results can be achieved

Scheme 2. Mechanism of CTV Formation

with iodotrimethylsilane.²⁶ The product is soluble in methanol and ethanol, but an attempt to recrystallize it from these solvents was unsuccessful. When crystallized from an ethanol/water mixture, CTC forms a stable complex with water in a 1:3 ratio.¹¹ The complexed water can only be removed under vacuum at high temperature. Hygroscopic CTC crystals eventually turn dark red in air. It is therefore necessary to store the product under a dried nitrogen atmosphere. The CTC's phenolic hydrogens can be readily observed for the CTC:water complex, but the signal is significantly broadened for the dried sample.

Side Chains

Preparation of the side chains constituted the bulk of my synthetic efforts. Flexible alkyl substituents were connected to the benzoate ring via ether linkages to form the acid precursors. A general reaction scheme is illustrated in Scheme 3. There are several methods for the synthesis of unsymmetrical ethers,²⁷ including the classic Williamson procedure.²⁸ Due to its mild condition and reported high yields, the potassium hydroxide (KOH)-dimethylsulfoxide (DMSO) system^{29,30} was chosen for this work.

Synthesis of Monoalkyloxybenzoic Acids

Methyl-*p*-hydroxybenzoate was used to prepare the mono-substituted side chains from the corresponding alkyl bromides. Potassium hydroxide in the powdered or pellet form can be used with comparable effectiveness. Maintaining anhydrous reaction conditions is also not necessary. The reaction is relatively fast and clean at room temperature. The product can be isolated by precipitation with water. Extraction with methylene chloride is an alternative route, but excessive foaming can be a problem. As a trade-off for the convenience of this method, the general yield of the acid from KOH-DMSO system, however, is below 50 %. Demethylation of the methylbenzoate group is a side-reaction that leads to a convenient deprotection step with subsequent addition of water to the same reaction vessel. This

deprotection route, however, only works for products with short alkyl substituents (chain lengths of ten carbons or less). The longer alkylated products tend to precipitate out of the mixture, preventing further reaction. Ester formation between the deprotected benzoate group and the excess alkyl bromide is another side reaction occurring after a prolonged reaction time.²⁹

Scheme 3. Synthesis of Alkoxylbenzoate Side Chains

Synthesis of Dialkyloxybenzoic Acids

The unprotected 3,4- and 3,5-dihydroxybenzoic acids were used for these two series of compounds. The salts of dihydroxy acids are less soluble in DMSO. To a greater extent, the resulting dialkyl substituted products also tend to be less soluble in common solvents. Prolonged reaction times may lead to ester formation as reported.²⁹ This side reaction is especially fast with the cyano-containing bromide, probably due to the greater solubility of the dicyanoalkyloxybenzoate product. Side product formation can be minimized with shorter reaction times and exact stoichiometric ratios of the alkyl bromide to the dihydroxy acid. If excess alkyl bromide is used, a subsequent deprotection step is necessary to reform the carboxylic acid from its ester.

Hexaesters of Cyclotricatechylene

Synthesis of Bowlic Liquid Crystals

The substituted benzoic acid side chains were first converted to the corresponding acid chlorides by reacting with excess thionyl chloride (SOCl_2). After distilling and purging the reaction mixture with nitrogen to remove the residual thionyl chloride, the resulting acid chlorides (ranging from viscous liquids to low melting solids) obtained were of acceptable purity and were used directly for the esterification step.

Attempts to synthesize hexaesters in anhydrous THF or ether with triethylamine lead to the formation of many side products and very low yields. In the presence of excess pyridine,¹³ CTC reacts with the monosubstituted benzoyl chloride to give reasonable yields (46-49 %) of the products. For the disubstituted and cyano-containing side chains, however, low yields were obtained (15-20 %).

The lower yields from the latter reactions were partly due to their small scale, which lead to difficult purifications. The use of an insufficiently dried batch of CTC also contributes to lower yields. For the more hydrophobic 4-tetradecyloxybenzoyl chloride and the 3,4-didodecyloxybenzoyl chloride, solubility seemed to have been a problem. These acid chlorides precipitated upon the addition of the pyridine/CTC mixture. Alternative reaction conditions using dichloromethane, dicyclohexylcarbodiimide and *p*-(dimethylamino)-pyridine⁸ would probably give better results for the longer mono- or disubstituted benzoate side chains.

Gel permeation chromatography (GPC) served as a convenient method for monitoring the reaction and for determining the purity of the products. GPC data showed that the major contaminants in the crude products were the unreacted acids. No intermediate acylation products such as triester or tetraester were detected (Figure 6). Despite the relatively clean reaction, multiple passes through neutral aluminum oxide were necessary to remove the excess acid. The cyanosubstituted esters were contaminated with a colored compound that could not be separated from the mixture by column chromatography. Literature procedures reported the use of silica gel,³ or the more efficient thick layer chromatography (TLC) technique.^{8, 13}

Standard spectroscopic data confirm the structure of the products. The proton signals from the CTV core can readily be observed in the ¹H-NMR spectrum, along with that of the side chains (Table I). It is interesting to note that for the free 3,4-disubstituted benzoic acid, the proton signals for the α and β methylene groups almost merge into each other. After being connected to the CTV core, however, these signals resolved into distinct peaks.

Figure 6. Representative GPC data for the acylation of CTC.

Table 1. ¹H-NMR Data of the Hexaesters

	<u>CTV Core</u>		<u>Side Chain</u>	
	He	Ha	H-Ar	
1a-d	3.85, d (3H)	4.92, d (3H)	7.39, s (6H)	$\text{CH}_3\text{---}(\text{CH}_2)_n\text{---CH}_2\text{---O---}$ 0.88, t (18H) 1.20-1.50 (2n x 6H) 1.77, qn (12H) 3.95, t (12H) 6.80, d (12H) 7.97, d (12H)
1e	3.85, d (3H)	4.92, d (3H)	7.39, s (6H)	$\text{CN---CH}_2\text{---CH}_2\text{---}(\text{CH}_2)_2\text{---CH}_2\text{---O---}$ 2.36, t (12H) 1.68, qn (12H) 1.40-1.60 (24H) 1.80, qn (12H) 3.97, t (12H) 6.81, d (12H) 7.98, d (12H)
2a	[3.76-3.93] (3H)	4.94, d (3H)	7.39, s (6H)	$\text{CH}_3\text{---}(\text{CH}_2)_5\text{---CH}_2\text{---CH}_2\text{---O---}$ 0.90, t (36H) 1.20-1.53 (120H) 1.82, qn (12H-para) 4.00, t (12H-para) 6.76, d (6H1) 7.49, d (6H3)
2b	[3.95-3.81] (3H)	4.94, d (3H)	7.39, s (6H)	$\text{CN---CH}_2\text{---}(\text{CH}_2)_3\text{---CH}_2\text{---CH}_2\text{---O---}$ 2.31-2.11 (24H) 1.40-1.74 (72H) 1.85, qn (12H-para) 4.01, t (12H-para) 6.78, d (6H1) 7.48, d (6H3)
3	[3.72-3.88] (3H)	4.95, d (3H)	7.43, s (6H)	$\text{CH}_3\text{---}(\text{CH}_2)_5\text{---CH}_2\text{---CH}_2\text{---O---}$ 0.88-0.95 (36H) 1.15-1.50 (120H) 1.70, qn (24H) 3.72-3.88 (24H) 6.59, d (6H1) 7.14, d (12H2,3)

Synthesis of Hexaacid Anchoring Agent

Several attempts to synthesize the hexaacid template for the alignment of bowlic liquid crystals resulted in the formation of intractable materials. Direct alkylation of cyclotri-catechylene with ethyl bromoacetate using potassium hydroxide in dimethylsulfoxide, sodium hydride in dimethylformamide, and potassium carbonate and/or sodium bicarbonate in dimethylacetamide were all unsuccessful. Ethyl bromoacetate might not be a suitable alkylating agent for the desired reaction. Low solubility of this highly polar compound in organic solvents might also be an issue. A detailed procedure for the preparation of a hexaacid with longer alkyl ether linkages to the cyclotrimeratrylene core is available in the literature.³¹

Liquid Crystalline Behaviors of the Hexaesters

The presence of mesophases can be observed under an optical microscope equipped with cross-polarizers. A thin sample was coated onto a clean microscope slide and heated to 200 °C then cooled down at a rate of 5 °C/min. If a sample is mesogenic, birefringent regions would start to grow in a characteristic pattern upon cooling below the isotropic temperature.^{8, 13} Optical microscopy data for the hexaesters are listed in Table II.

Compounds **1a-d** are birefringent at room temperature. Upon cooling from the isotropic phase, mesogenic transitions were observed. The transition temperature of **1c** was 5 °C lower than the reported value.^{13, 16} This could be the result of supercooling due to the relatively fast cooling rate. As the aliphatic chain length in this series increases from eight to twelve carbons (**1a-c**), the mesophase-to-isotropic transition temperature increases. The lower crystalline-to-mesophase transitions for compounds with longer side chains are also expected to be depressed, resulting in an overall wider mesomorphic temperature

range. An attempt to crystallize **1c** was reported to be unsuccessful,¹³ while **1a** was observed to crystallize upon very slow evaporation of solvent over an extended period.

Table 2. Isotropic Transition Temperatures of the Hexaesters

Compound	Birefringence	T _{iso} (°C)
1a	yes	160
1b	yes	177
1c	yes	183
1d (=1a + 1b)	yes	176
1e	no	none
2a	no	none
2b	no	186
3	no	none

Compound **1d** is a hybrid hexaester containing a 1:1 mixture of 4-octyloxybenzoate and 4-decylbenzoate side chains. This mixed ester exhibits an isotropic transition temperature very close to that of **1b**. ¹H-NMR integration gave, as expected, an average alkyl chain length of about 9 carbons. The cyano substituted **1e**, on the other hand, did not form a mesophase and eventually turned dark at high temperatures.

The 3,4-disubstituted benzoate hexaester derivative (**2b**), which contains an ω-cyano group, was found to be non-birefringent. The possibility of a mesomorphic transition below room temperature cannot be ruled out for the cyano based compounds, since they are

highly viscous, transparent liquids at 25 °C. Compared with the **1a** analog, the disubstituted side chain raises the isotropic transition of **2a** significantly. This compound, however, is not birefringent at room temperature. The mesophase formation can only be induced after slow cooling from the isotropic phase (monotropic). The branched side chains of **2a** are probably bulky enough to interfere with efficient stacking of the core, leading to the monotropic behavior.

In the case of **3**, a 3,5-disubstituted benzoate hexaester, no mesophases were detected upon the heating and cooling cycle. The 3,5-disubstituted pattern could have created sufficient steric hindrance to retard or prevent the stacking of the cores altogether, resulting instead in a glassy solid state.

In a poor solvent such as mixed hexanes, the hexaesters **1a-d** form highly viscous solutions. This behavior may be caused by the self-assembling of the molecules into extended, more tightly associated polymer-like columns. Thus these compounds may be induced to form ordered aggregates in selected solvent (lyotropic behavior). Similar behavior of the discotic mesogens has been observed.³²

Alignment of the Mesophases

X-ray evidence has shown that compound **1c** forms a disordered hexacolumnar mesophase.¹⁶ This arrangement is caused by the CTV cones pointing in opposite direction within a column and thus is not ferroelectric. Realignment of the CTV core can be achieved via the umbrella-like inversion of the cone at high temperature, under the directing influence of an external electro/magnetic field.⁸ The cyano-containing esters are expected to have a greater dipole moment along its axis. These compounds can be utilized as additives to aid in electro-switching. Instead of alignment with the hexaacid template, the polar

substrate can be treated with octadecyltriethoxysilane¹⁴ to form a nonpolar surface. The nonpolar alkyl side chains then could anchor onto the treated surface, forming perpendicular columns. If confirmed, the lyotropic behavior of CTV based liquid crystals could also be utilized to align the molecules in the less viscous solution state.

SUMMARY

Synthetic procedures for CTV, CTC, and alkyloxybenzoate side chains were established. A series of corresponding CTV hexaesters were synthesized. Room temperature liquid crystalline behaviors were observed for the monosubstituted alkyloxybenzoate esters (**1a-d**). Increasing the alkyl chain lengths resulted in higher isotropic transition temperatures. Mesophases were not observed for hexaesters with dialkyl substituted (**2b, 3**) and cyano-terminated side chains (**1e**), except **2a** which exhibited monotropic behavior.

The synthesis of a mixed hexaester with different chain lengths was demonstrated. This approach could be utilized to incorporate a fraction of cyano-terminated side chains into CTV-based liquid crystals to facilitate the alignment process without severely altering their mesomorphic behaviors.

EXPERIMENTAL SECTION

General Procedures

The melting points were measured using a MEL-TEMP apparatus (Laboratory Devices). The IR spectra were recorded on a Bio Rad FTS-60A spectrophotometer, using thin films of the samples on sodium chloride plates. The ¹H-NMR spectra were recorded on a GE

QE-300 spectrometer; chemical shifts are expressed in ppm downfield from an internal tetramethylsilane (0.00 ppm) reference. Gel permeation chromatography (GPC) was performed with a Hewlett-Packard 1090 liquid chromatograph instrument equipped with Chemstation HP7999A GPC software and a series of four Polymer Labs PL-Gel columns (100, 500, 10^3 and 10^4 Å pore diameters) using THF as eluent at 1 mL/min rate and polystyrene standards for the calibration.

For microscopic analysis, a thin film of sample was smeared onto a glass slide and heated above the isotropic transition temperature on a Mettler hot stage. As the sample was cooled at a rate of 5 °C/min., the appearance of mesogenic phases were observed using cross-polarizers.

Cyclotrimeratrylene (CTV)^{22, 23}

Concentrated sulfuric acid (77 mL, 785.1 mmol) was diluted with water (33 mL), to form a 70% v/v aqueous solution, then chilled to 15 °C. To the chilled acid solution, veratrole (30.00 g, 217.1 mmol) was added. The resulting light yellow solution was transferred to a 125-mL addition funnel fitted with a nitrogen line.

To a 500-mL, three necked flask equipped with a mechanical stirrer and a thermometer, aqueous formaldehyde solution (42.00 g of 37% w/v, 517.5 mmol) was added and chilled to 0 °C (± 3 °C) with an ice-salt bath. The addition funnel containing the chilled acidic veratrole solution was then fitted to the flask, and the dropwise addition began with vigorous stirring. The temperature during the addition (~ 1 hour) was maintained between 0 and 3 °C. A white precipitate formed initially. Toward the end of the addition, the reaction mixture thickened and turned a pastel purple color. Stirring became very difficult. The reaction mixture was then allowed to stir under nitrogen overnight. Water (100 mL)

was added to the reaction flask with stirring to dilute the thick mixture. The crude product was collected using a 350-mL medium fritted glass funnel. Filtering was very slow due to the fine nature of the precipitate. The filter cake was washed with water (400 mL) then a saturated aqueous sodium bicarbonate solution (150 mL). As a result of the washings, the precipitate turned from light purple to light yellow. The crude product was then redissolved in dichloromethane (200 mL) and washed with water (5x100 mL) in a 500-mL separatory funnel. The cloudy, reddish-orange organic layer was dried (MgSO_4), decolorized (activated charcoal), and filtered. The organic solvent from the filtrate was removed under reduced pressure at 25 °C to yield a light yellow solid. The crude product was dissolved in a minimal amount of boiling dichloromethane and poured into boiling ethyl acetate (200 mL). The solution was filtered hot and then chilled in the freezer overnight to recrystallize the product as white needles (21.5 g, 66 %): mp 235-8 °C (lit.²³ mp 234 °C). The filtrate can be further concentrated and recrystallized to yield a second crop of crystals (1.32 g, 4 %): mp 233-5 °C; IR: 2988, 2934, 2902, 2844, 2826, 1608, 1513, 1464, 1394, 1343, 1262, 1222, 1194, 1149, 1090, 996, 850, 739 cm^{-1} ; $^1\text{H-NMR}$ (DMSO-d_6): 3.52 (d, 3H, $J = 13$ Hz, CH_2 pseudo-equatorial) 3.71 (s, 18H, $-\text{O}-\text{CH}_3$), 4.70 (d, 3H, $J = 13$ Hz, $-\text{CH}_2$ pseudo-axial), 7.08 (s, 6H, Ar-H) ppm.

Cyclotricatechylene (CTC)^{10, 23}

CTV (20.00 g, 44.39 mmol) in dichloromethane (200 mL) was added to a 1-L, three necked flask equipped with a mechanical stirrer, a nitrogen line and a septum inlet. The flask was purged with nitrogen for 15 min. Boron tribromide (300.0 mL of a 1.0 M solution in dichloromethane, 300.0 mmol) was added via the septum inlet as a slow stream via a Teflon cannula, using positive nitrogen pressure. The solution turned reddish-brown at the beginning of the addition, followed by the formation of a brown precipitate. The reaction mixture was stirred at room temperature for 3 h. A Tygon tube was connected

from the head space above the reaction mixture to a stirred KOH solution which was used to trap the HBr evolved during workup. Water was then added to the mixture in small portions with stirring until the gas ceased to evolve. Additional water was added until the thick precipitate aggregated and separated from the solution. Dichloromethane was then removed by vacuum filtration. The crude product was washed with water (300 mL), and the wet filter cake redissolved in boiling ethanol (250 mL). After the dark, insoluble materials were filtered out of the ethanolic solution, the filtrate was concentrated under reduced pressure at 80 °C to half of the initial volume. Water (300 mL) was added to the residue and the mixture was heated to reflux in a water bath. The remaining ethanol was then removed from the mixture under reduced pressure to precipitate the product. After the aqueous mixture was refrigerated overnight, the product was collected by filtration, washed with water, then vacuum dried to give a beige powder (13.7 g, 84 %): mp > 300 °C (decomp.); IR: 3305 (br), 1696, 1612, 1520, 1441, 1356, 1283, 1245, 1174, 1131, 1068, 889, 858, 746 cm⁻¹; ¹H-NMR (DMSO-d₆): 3.21 (d, 3H, *J* = 13 Hz, -CH₂ pseudo-equatorial), 4.48 (d, 3H, *J* = 13 Hz, -CH₂ pseudo-axial), 6.66 (s, 6H, Ar-H), 8.60 (s, broad, 6H, -OH, absent for vacuum dried sample) ppm.

4-Octyloxybenzoic acid (4-C8 acid)

To a 100-mL flask equipped with a nitrogen line, methyl-*p*-hydroxybenzoate (8.00 g, 52.6 mmol), powdered KOH (6.49 g, 116 mmol) and DMSO (50 mL) were added and stirred at room temperature for 10 min. 1-Bromooctane (13.96 g, 63.10 mmol) was added slowly to the light yellow mixture. A white precipitate formed about 5 min after the addition. The mixture was stirred under nitrogen overnight at room temperature. At the end of the reaction time, water (30 mL) was added and the mixture stirred at 80 °C for 2 h. The mixture was then acidified to pH 3 and extracted with dichloromethane (4 x 25 mL). Excessive foaming occurred during the extraction. The combined extracts were then dried

(MgSO₄), filtered and concentrated. Recrystallization of the resulting residue from THF/petroleum ether to give white needles (7.12 g, 48 %): mp 99-101 °C; IR: 2951(br), 2927 (br), 2850 (br), 2674 (br), 2560 (br), 1690, 1608, 1428, 1296, 1255, 1170, 959, 849, 771 cm⁻¹; ¹H-NMR (DMSO-d₆): 0.86 (t, 3H, *J* = 6.5 Hz, -CH₃), 1.15-1.55 (m, 10H, -CH₂-), 1.72 (quintet, 2H, *J* = 7.0 Hz, β-CH₂-), 4.00 (t, 2H, *J* = 7.0, -O-CH₂-), 7.00 (d, 2H, *J* = 8.5 Hz, Ar-H), 7.93 (d, 2H, *J* = 8.5 Hz, Ar-H), 12.65 (s, broad, 1H, -OH) ppm. Anal. Calcd for C₁₅H₂₂O₃: C, 71.97; H, 8.86. Found: C, 71.96; H, 8.98.

4-Decyloxybenzoic acid (4-C10 acid)

The procedure for the 4-C8 acid was followed with methyl-4-hydroxybenzoate (14.00 g, 92.01 mmol), 1-bromodecane (25.00 g, 113.0 mmol), powdered KOH (7.79 g, 139 mmol) and DMSO (50 mL) as starting materials. After the deprotection, the reaction mixture was acidified to pH 3. The white precipitate was filtered, washed and dried then recrystallized from THF/petroleum ether to avoid the extraction. The purified product is a white powder (13.2 g, 41 %): mp 95-97 °C; IR: 2931 (br), 2854 (br), 2665 (br), 2564 (br), 1681, 1607, 1580, 1514, 1470, 1432, 1333, 1308, 1259, 1171, 939, 846, 771 cm⁻¹; ¹H-NMR (DMSO-d₆): 0.89 (t, 3H, *J* = 6.5 Hz, -CH₃), 1.20-1.52 (m, 14H, -CH₂-), 1.80 (quintet, 2H, *J* = 7.0 Hz, β-CH₂-), 4.02 (t, 2H, *J* = 7.0 Hz, -O-CH₂-), 6.94 (d, 2H, *J* = 8.5 Hz, Ar-H), 8.06 (d, 2H, *J* = 8.5 Hz, Ar-H) ppm. Anal. Calcd for C₁₇H₂₆O₃: C, 73.35; H, 9.41. Found: C, 73.46; H, 9.81.

4-Dodecyloxybenzoic acid (4-C12 acid)

The procedure for the 4-C10 acid was followed with methyl-4-hydroxybenzoate (14.00 g, 92.01 mmol), 1-bromododecane (27.52 g, 110.4 mmol), KOH pellets (11.36 g, 202.4 mmol) and DMSO (50 mL) as starting materials. After the reaction time, the reaction

mixture was acidified to ~ pH 3. The crude product was filtered, washed with water and then refluxed in THF (20 mL) and 30% KOH aqueous solution (20 mL) for 2 h. The resulting greenish-yellow cloudy solution was filtered and acidified with concentrated hydrochloric acid. The precipitate was filtered, washed with water, suction dried then recrystallized from a THF/petroleum ether (1:1) mixture to give a white powder (13.2 g, 47 %): mp 190-92 °C; IR: 2954 (br), 2919, 2850, 1673, 1606, 1469, 1306, 1257, 1171, 1023, 859, 782 cm^{-1} ; $^1\text{H-NMR}$ (DMSO-d_6): 0.89 (t, 3H, $J = 6.5$ Hz, $-\text{CH}_3$), 1.25-1.45 (m, 18H, $-\text{CH}_2-$), 1.80 (quintet, 2H, $J = 7.0$ Hz, $\beta\text{-CH}_2-$), 4.02 (t, 2H, $J = 7.0$ Hz, $-\text{O-CH}_2-$), 6.93 (d, 2H, $J = 8.5$ Hz, Ar-H), 8.03 (d, 2H, $J = 8.5$ Hz, Ar-H) ppm. Anal. Calcd for $\text{C}_{19}\text{H}_{30}\text{O}_3$: C, 74.47; H, 9.87. Found: C, 69.16; H, 9.36. The sample submitted for elemental analysis came from the second crop of the recrystallization. The inferior purity is probably responsible for the discrepancy between the actual and the theoretical values.

4-(6-Cyanohexyloxy)benzoic acid (4-C6CN acid)

To a 100-mL round flask equipped with a nitrogen line, methyl-4-hydroxybenzoate (5.00 g, 32.86 mmol), 7-bromoheptanenitrile (7.00 g, 36.81 mmol), KOH pellets (5.53 g, 98.59 mmol) and DMSO (30 mL) were added. The yellowish mixture was stirred at 80 °C for 3 h under nitrogen. By the end of the reaction time, the KOH pellets had dissolved with the formation of a small amount of a white precipitate. Water (10 mL) was then added, and the mixture stirred overnight to deprotect the methylated benzoate group. The mixture was then filtered and acidified (0.1 N HCl) to ~ pH 3. The precipitate was filtered, washed with water, suction dried, then recrystallized from acetone to yield a white powder (5.20 g, 64 %): mp 136-8 °C; IR: 3433 (br), 3065 (br), 2941 (br), 2859 (br), 2677 (br), 2564 (br).

2244 (-CN), 1681, 1604, 1514, 1430, 1324, 1295, 1279, 1256, 1173, 981, 931, 851. 770 cm^{-1} ; $^1\text{H-NMR}$ (DMSO-d_6): 1.30-1.80 (m, 8H, $-\text{CH}_2-$), 2.50 (t, 2H, $J = 7.0$ Hz, $-\text{CH}_2-\text{CN}$), 4.03 (t, 2H, $J = 6.5$ Hz, $-\text{CH}_2-\text{O}$) 7.01 (d, 2H, $J = 8.5$ Hz, Ar-H), 7.90 (d, 2H, $J = 8.5$ Hz, Ar-H) ppm. Anal. Calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_3$: C, 67.00; H, 6.93; N, 5.66. Found: C, 66.74; H, 7.29; N, 5.39.

3,4-Dioctyloxybenzoic acid (3,4-C8 acid)

To a 100-mL, pear-shaped flask equipped with a magnetic stirrer and a nitrogen line, 3,4-dihydroxybenzoic acid (3.00 g, 19.47 mmol) and DMSO (30 mL) were added. After the acid dissolved, powdered KOH (3.50 g, 63.29 mmol) followed by 1-bromooctane (8.65 g, 44.77 mmol) were added. The mixture was heated to 70 $^{\circ}\text{C}$ and stirred under nitrogen for 16 h. After the reaction time, water (10 mL) was added and the mixture heated for an additional 3 h. The reaction mixture was then acidified with 0.1 N hydrochloric acid. The white precipitate was filtered, washed with water then suction dried. The crude product was recrystallized from dichloromethane to give a white powder (3.20 g, 43 %): mp 122-124 $^{\circ}\text{C}$; IR: 2924, 2851, 1669, 1594, 1466, 1441, 1307, 1277, 1227, 1141, 1068, 940, 869, 769 cm^{-1} ; $^1\text{H-NMR}$ (DMSO-d_6): δ 0.89 (t, 6H, $J = 6.5$ Hz, $-\text{CH}_3$), 1.20-1.55 (m, 20H, $-\text{CH}_2-$), 1.79-1.92 (m, 4H, $\beta\text{-CH}_2-$), 4.03-4.11 (m, 4H, $-\text{CH}_2-\text{O}-$), 6.90 (d, 1H, $J = 8.5$ Hz, Ar-H), 7.60 (s, 1H, Ar-H), 7.73 (d, 1H, $J = 8.5$ Hz, Ar-H) ppm. Anal. Calcd for $\text{C}_{23}\text{H}_{38}\text{O}_4$: C, 72.98; H, 10.12. Found: C, 73.01; H, 10.42.

3,4-Bis(6-cyanoheptyloxy)benzoic acid (3,4-C6CN acid)

The procedure for 3,4-C8 acid was followed with 3,4-dihydroxybenzoic acid (2.00 g, 12.98 mmol), 7-bromoheptanenitrile (5.67 g, 29.85 mmol), KOH pellet (2.33 g, 41.53 mmol) as starting materials in DMSO (15 mL). At the end of the reaction time, water (5

mL) was added, and the mixture heated at 80 °C for 3 h. The mixture separated into three layers: a light yellow oily top layer, a dark reddish-brown organic middle layer, and a lighter brown bottom aqueous layer. After being acidified to pH 4 with concentrated hydrochloric acid, the mixture was extracted with dichloromethane (3 x 20 mL), washed with deionized water (2 x 30 mL), dried and concentrated under reduced pressure at 35 °C. The crude product was recrystallized from acetone to yield white crystals (2.14 g, 44 %): mp 120-122 °C; IR: 2945 (br), 2863 (br), 2627 (br), 2545 (br), 2243 (-CN), 1673, 1595, 1520, 1443, 1350, 1279, 1226, 1136, 1109, 982, 874, 766 cm⁻¹; ¹H-NMR (DMSO-d₆): δ 1.45-1.64 (m, 8H), 1.71 (quintet, *J* = 5 Hz, 4H), 1.79-1.95 (m, 4H), 2.37 (t, 4H, *J* = 6.5 Hz, -CH₂-CN), 4.02-4.13 (m, 4H, -CH₂-O-), 6.90 (d, 1H, *J* = 8.5 Hz, Ar-H), 7.59 (d, 1H, *J* = 2.0 Hz, Ar-H), 7.75 (dd, 1H, *J* = 2.0, 8.5 Hz, Ar-H) ppm. Anal. Calcd for C₂₃H₁₈O₄: C, 72.98; H, 10.12. Found: C, 73.01; H, 10.42.

3,5-Dioctyloxybenzoic acid (3,5-C8 acid)

The procedure for 3,4-C8 acid was followed with 3,5-dihydroxybenzoic acid (3.00 g, 19.47 mmol), 1-bromooctane (7.71 g, 39.90 mmol), KOH pellets (3.5 g, 62.29 mmol) as starting materials in DMSO (20 mL). The final reaction mixture separated into a bottom aqueous layer and an oily top portion. Following the separation, the product slowly recrystallized (after 2 weeks at 25 °C) from the top oil to give a low melting solid (7.5 g, 34 %): mp 54-55 °C; IR: 2958 (br), 2924 (br), 2871 (br), 2853 (br), 2637 (br), 1691, 1612, 1445, 1423, 1392, 1320, 1272, 1171, 1063, 941, 857, 738 cm⁻¹; ¹H-NMR (DMSO-d₆): δ 0.85 (t, 6H, *J* = 6.5 Hz, -CH₃), 1.15-1.60 (m, 20H, -CH₂-), 1.70 (quintet, 4H, *J* = 6.5 Hz, b-CH₂-), 3.95 (t, 4H, *J* = 6.5 Hz, -O-CH₂-), 6.68 (d, 1H, *J* = 1.5 Hz, Ar-H), 7.03 (d, 2H, *J* = 1.5 Hz, Ar-H) ppm. Anal. Calcd for C₂₃H₃₈O₄: C, 72.98; H, 10.12. Found: C, 72.94; H, 10.53.

Hexa(4-octyloxybenzoyl)cyclotricatechylene (1a)

A 50-mL pear-shaped flask was equipped with a magnetic stirrer and a drying tube connected by a length of Tygon tubing whose other end was submerged in a 20% aqueous potassium hydroxide solution for the absorption of the sulfur dioxide by-product. 4-Octyloxybenzoic acid (5.00 g, 19.97 mmol) and thionyl chloride (10 mL, 84 mmol) were added to the reaction flask. The mixture was heated to 80 °C in an oil bath with stirring. Sulfur dioxide gas started to evolve from the reaction mixture. After 1 h, the acid was completely dissolved, resulting in a greenish-yellow liquid. Excess thionyl chloride was then distilled from the reaction mixture at atmospheric pressure. The residue was stirred at 100 °C for an additional 30 min with nitrogen purging to remove most of the thionyl chloride. The crude product was then utilized for subsequent synthesis without further purification.

To the crude acid chloride, a slurry of CTC (0.91 g, 2.50 mmol) in pyridine (5 mL) was added in small portions at 80 °C. The mixture was stirred under nitrogen overnight. At the end of the reaction time, pyridine was removed under reduced pressure at 90 °C. The residue was redissolved in dichloromethane (25 mL). After washing with water (4 x 20 mL), the cloudy organic fraction was dried (MgSO_4), then the organic solvent was removed from the filtered solution under reduced pressure at 35 °C. The residue was again redissolved in a minimal amount of boiling acetone. The excess acid starting material precipitated out as colorless needles upon cooling and was removed by filtration. The concentrated filtrate was then chromatographed through neutral aluminum oxide (150 g) packed in a 4 cm i.d. glass column, using acetone (~250 mL) as eluent to give a slightly yellow waxy solid. The solid was redissolved in dichloromethane and chromatographed again through neutral aluminum oxide (20 g) packed in a 2 cm i.d. glass column using

dichloromethane (50 mL) as the eluent. After the removal of the eluent, an off-white, waxy solid was obtained (2.13 g, 48 %): T_{iso} 160 °C; IR: 2927, 2856, 1734, 1607, 1581, 1511, 1469, 1313, 1256, 1170, 1133, 1075, 1031, 846, 762, 692 cm^{-1} ; 1H -NMR ($CDCl_3$): 0.88 (t, 18H, $J = 6.0$ Hz), 1.20-1.50 (m, 60H), 1.77 (quintet, 12H, $J = 6.0$ Hz), 3.85 (d, 3H, $J = 13$ Hz), 3.95 (t, 12H, $J = 6.0$ Hz), 4.92 (d, 3H, $J = 13$ Hz), 6.80 (d, 12H, $J = 9.0$ Hz), 7.39 (s, 6H), 7.97 (d, 12H, $J = 9.0$ Hz) ppm. Anal. Calcd for $C_{111}H_{138}O_{18}$: C, 75.74; H, 7.90. Found: C, 75.79; H, 8.07.

Hexa(4-decyloxybenzoyl)cyclotricatechylene (1b)

The procedure for **1a** was repeated with 4-decyloxybenzoic acid (8.00 g, 28.73 mmol), thionyl chloride (20 mL, ~ 168 mmol), CTC (1.32 g, 3.59 mmol), in pyridine (15 mL). After repeated column chromatography through neutral alumina with dichloromethane elution, a translucent, waxy solid was obtained (3.26 g, 47 %): T_{iso} 177 °C; IR: 2926, 2855, 1734, 1607, 1511, 1257, 1171, 1088, 1075, 846, 762 cm^{-1} ; 1H -NMR ($CDCl_3$): 0.88 (t, 18H, $J = 6.0$ Hz), 1.20-1.50 (m, 84H), 1.77 (quintet, 12H, $J = 6.0$ Hz), 3.85 (d, 3H, $J = 13$ Hz), 3.95 (t, 12H, $J = 6.0$ Hz), 4.92 (d, 3H, $J = 13$ Hz), 6.80 (d, 12H, $J = 9.0$ Hz), 7.39 (s, 6H), 7.97 (d, 12H, $J = 9.0$ Hz) ppm. Anal. Calcd for $C_{123}H_{162}O_{18}$: C, 76.60; H, 8.47. Found: C, 76.44; H, 8.67.

Hexa(4-dodecyloxybenzoyl)cyclotricatechylene (1c)^{13, 16}

The procedure for **1a** was repeated with 4-dodecyloxybenzoic acid (8.00 g, 26.10 mmol), thionyl chloride (20 mL, ~168 mmol) and CTC (1.37 g, 3.73 mmol) in pyridine (15 mL). After repeated column chromatography through neutral alumina with dichloromethane elution, a translucent, waxy solid was obtained (3.57 g, 46 %): T_{iso} 183 °C (lit.^{13, 16} T_{iso} 188 °C); IR: 2925, 2854, 1734, 1607, 1580, 1511, 1468, 1313, 1257, 1171, 1134, 1087, 1075, 1008, 847, 762 cm^{-1} ; 1H -NMR ($CDCl_3$): 0.88 (t, 18H, $J = 6.0$ Hz), 1.20-

1.50 (m, 108H), 1.77 (quintet, 12H, $J = 6.0$ Hz), 3.85 (d, 3H, $J = 13$ Hz), 3.95 (t, 12H, $J = 6.0$ Hz), 4.92 (d, 3H, $J = 13$ Hz), 6.80 (d, 12H, $J = 9.0$ Hz), 7.39 (s, 6H), 7.97 (d, 12H, $J = 9.0$ Hz) ppm. Anal. Calcd for $C_{135}H_{186}O_{18}$: C, 77.33; H, 8.94. Found: C, 77.21; H, 9.25.

Hexaester of mixed chain length (1d)

The procedure for **1a** was repeated with a mixture of 4-octyloxybenzoic acid (2.00 g, 7.99 mmol), of 4-decyloxybenzoic acid (2.22 g, 7.99 mmol), thionyl chloride (20 mL, ~168 mmol), and CTC (0.84 g, 2.28 mmol) as starting materials in pyridine (15 mL). After repeated column chromatography through neutral alumina with dichloromethane elution, a translucent, waxy solid was obtained (1.85 g, 46 %): T_{iso} 176 °C; IR: 2926, 2856, 1734, 1607, 1581, 1511, 1470, 1314, 1257, 1170, 1134, 1087, 1075, 1009, 847, 762 cm^{-1} ; 1H -NMR ($CDCl_3$): 0.88 (t, 18H, $J = 6.0$ Hz), 1.20-1.50 (m, 75H), 1.77 (quintet, 12H, $J = 6.0$ Hz), 3.85 (d, 3H, $J = 13$ Hz), 3.95 (t, 12H, $J = 6.0$ Hz), 4.92 (d, 3H, $J = 13$ Hz), 6.80 (d, 12H, $J = 9.0$ Hz), 7.39 (s, 6H), 7.97 (d, 12H, $J = 9.0$ Hz) ppm. Anal. Calcd for $C_{117}H_{150}O_{18}$: C, 76.19; H, 8.20. Found: C, 76.14; H, 8.46.

Hexa[(4-(6-cyanohexyloxy)benzoyl)cyclotricatechylene] (1e)

The procedure for **1a** was repeated with 4-(6-cyanohexyloxy)benzoic acid (4.00 g, 16.17 mmol), thionyl chloride (20 mL, ~168 mmol), and CTC (0.74 g, 2.02 mmol) as starting materials in pyridine (15 mL). After repeated column chromatography through neutral alumina with dichloromethane elution, a yellowish waxy solid was obtained (0.57 g, 16 %): IR: 2940, 2866, 2245, 1737, 1607, 1511, 1257, 1168, 1070, 1006, 845, 761 cm^{-1} ; 1H -NMR ($CDCl_3$): 1.40-1.60 (m, 24H), 1.68 (q, 12H, $J = 6.0$ Hz), 1.80 (quintet, 12H, $J = 6.0$ Hz), 2.36 (t, 12H, $J = 6.0$ Hz), 3.86 (d, 3H, $J = 13$ Hz), 3.97 (t, 12H, $J = 6.0$ Hz), 4.93 (d, 3H, $J = 13$ Hz), 6.81 (d, 12H, $J = 9.0$ Hz), 7.39 (s, 6H), 7.98 (d, 12H,

$J = 9.0$ Hz) ppm. Anal. Calcd for $C_{105}H_{108}N_6O_{18}$: C, 72.40; H, 6.25; N, 4.82. Found: C, 68.89; H, 7.03; N, 3.59. The elemental analysis values do not agree well with the theoretical calculation due to the difficulty in purification for this sample.

Hexa[(3,4-octyloxy)benzoyl]cyclotricatechylene (2a)

The procedure for **1a** was repeated with 3,4-dioctyloxybenzoic acid (3.00 g, 7.92 mmol), thionyl chloride (10 mL, ~ 84 mmol), CTC (0.36 g, 0.99 mmol), and pyridine (10 mL). After repeated column chromatography through neutral alumina with dichloromethane elution, a translucent, waxy solid was obtained (0.50 g, 20 %): T_{iso} 186 °C; IR: 2925, 2854, 1739, 1721, 1600, 1518, 1468, 1427, 1397, 1346, 1272, 1209, 1192, 1132, 1080, 976, 908, 750 cm^{-1} ; 1H -NMR ($CDCl_3$): 0.90 (m, 36H), 1.20-1.50 (m, 120H), 1.74 (quintet, 12H, $J = 6.0$ Hz), 1.82 (quintet, 12H, $J = 6.0$ Hz), 3.76-3.93 (m, 15H), 4.00 (q, 12H, $J = 6.0$ Hz), 4.94 (d, 3H, $J = 13$ Hz), 6.76 (d, 6H, $J = 8.0$ Hz), 7.40 (s, 6H), 7.49 (d, 6H, $J = 1.5$ Hz), 7.66 (dd, 6H, $J = 1.5, 8.0$ Hz) ppm. Anal. Calcd for $C_{159}H_{234}O_{24}$: C, 75.50; H, 9.32. Found: C, 74.66; H, 9.61.

Hexa{[3,4-bis-(6-cyanohexyloxy)benzoyl]}cyclotricatechylene (2b)

The procedure for **1a** was repeated with 3,4-bis(6-cyanohexyloxy)benzoic acid (2.00 g, 5.37 mmol), thionyl chloride (10 mL, ~ 84 mmol), CTC (0.25 g, 0.67 mmol) as starting materials in pyridine (15 mL). After repeated column chromatography through neutral alumina with dichloromethane elution, an amber waxy solid was obtained (0.3 g, 18 %): IR : 2939, 2865, 2245, 1734, 1599, 1514, 1429, 1271, 1206, 1177, 1132, 1085, 952, 752 cm^{-1} ; 1H -NMR ($CDCl_3$): 1.40-1.74 (m, 72H), 1.77 (quintet, 12H, $J = 6.0$ Hz), 1.85 (q, 12H, $J = 6.0$ Hz), 2.31-2.41 (m, 24H), 3.81-3.95 (m, 27H), 4.01 (t, 24H, $J = 6.0$ Hz), 4.94 (d, 3H, $J = 13$ Hz), 6.78 (d, 6H, $J = 8.0$ Hz), 7.39 (s, 6H), 7.48 (d, 6H,

$J = 1.5$ Hz), 7.68 (dd, 6H, $J = 1.5, 8.0$ Hz) ppm. Anal. Calcd for $C_{147}H_{174}N_{12}O_{24}$: C, 70.82; H, 7.03; N, 6.74. Found: C, 68.08; H, 7.55; N, 5.41. The elemental analysis values do not agree well with the theoretical calculation due to the difficulty in purification for this sample.

Hexa[(3,5-dioctyloxy)benzoyl]cyclotricatechylene (3)

The procedure for **1a** was repeated with 3,5-dioctyloxybenzoic acid (2.00 g, 5.28 mmol), thionyl chloride (10 mL, ~ 84 mmol), CTC (0.24 g, 0.66 mmol) as starting materials in pyridine (15 mL). After repeated column chromatography through neutral alumina with dichloromethane elution, an amber waxy solid was obtained (0.22 g, 13 %): IR: 2926, 2855, 1746, 1596, 1500, 1464, 1446, 1346, 1302, 1275, 1217, 1192, 1172, 1059, 839, 751 cm^{-1} ; $^1\text{H-NMR}$ (CDCl_3): 0.80-0.95 (m, 36H), 1.15-1.50 (m, 120H), 1.70 (quintet, 24H, $J = 6.0$ Hz), 3.72-3.88 (m, 27H), 4.95 (d, 3H, $J = 13$ Hz), 6.59 (d, 6H, $J = 1.5$ Hz), 7.14 (d, 12H, $J = 1.5$ Hz), 7.43 (s, 6H) ppm. Anal. Calcd for $C_{159}H_{234}O_{24}$: C, 75.50; H, 9.32. Found: C, 76.91; H, 10.18. The elemental analysis values do not agree well with the theoretical calculation due to the difficulty in purification for this sample.

REFERENCES

1. Chandrasekhar, S. *Liquid Crystals*. 2nd Ed. Cambridge University Press, Cambridge, 1992, pp. 1-16.
2. Ibid. p 393.
3. Zimmermann, H.; Poupko, R.; Luz, Z.; Billard, J. Z. *Natureforsch.*, **1985**, 40a, 149-160.
4. Mertesdorf, C.; Ringsdorf, H.; Stumpe, J. *Liquid Crystals*, **1991**, 9 (3), 337-357.
5. Lam, L. *Possible Liquid Crystalline High Tc Superconductors*. Proceeding of the Third Asia-Pacific Physics Conference, Hong Kong, June 20-24, 1988.
6. Pryce, D. "EDN Special Report", *EDN*, October 12, 1987. pp 103-114.
7. Brown, G.; Crocker, P. "Liquid Crystals--A colorful state of matter", *C&EN*, January 31, 1983, pp. 24-37.
8. Malthete, J.; Collet, A. *J. Am. Chem. Soc.*, **1987**, 109, 7544-7545.
9. Dalcanale, E.; Du Vosel, A.; Levelut, A. M.; Malthete, J. *Liquid Crystals*, **1991**, 10 (2), pp. 185-198.
10. Hyatt, A. J. *J. Org. Chem.*, **1978**, 43 (9), 1808.
11. Hyatt, A. J.; Duesler, E. N.; Curtin, D. Y.; Paul, I. C. *J. Org. Chem.*, **1980**, 45, 5074-5079.
12. Bonsignore, S.; Commetti, G.; Dalcanale, E.; Du Vosel, A. *Liquid Crystals*, **1990**, 8 (5), 639-649.
13. Malthete, J.; Collet, A. *Nouveau Journal De Chimie*, **1985**, 9 (3), 151-153.
14. Jakli, A.; Saupe, A.; Scherowsky, G.; Chen, X. *Abstract No. C2.003*. 16th International Liquid Crystal Conference. June 24-28, 1996.
15. Zimmermann, H.; Poupko, R.; Luz, Z.; Billard, J. Z. *Naturforsch.*, **1986**, 41a, 1137-1140.
16. Levelut, A.; Malthete, J.; Collet, A. *J. de Physique.*, **1986**, 47, 351-357.
17. Lehn, J. M.; Malthete, J.; Levelut, A. *J. Chem. Soc., Chem. Commun.*, **1985**, 1794.
18. Zimmermann, H.; Poupko, R.; Luz, Z.; Billard, J. *Liquid Crystals*, **1988**, 3 (6), 759-770.
19. Cometti, G.; Dalcanale, E.; Du Vosel, A.; Levelut, A. *Liquid Crystals*, **1992**, 11 (1), 93-100.

20. Bonsignore, S.; Du Vosel, A.; Guglielmetti, G.; Dalcanales, E.; Ugozzoli, F.; *Liquid Crystals*, **1993**, *13* (4), 471-482.
21. Buisine, J.; Zimmermann, H.; Pouko, R.; Luz, Z.; Billard, J. *J. Mol. Cryst. Liq. Cryst.*, **1987**, *151*, 391-398.
22. Robinson, G. M. *J. Chem. Soc.*, **1915**, 267, 267-276.
23. Lindsey, A. S. *J. Chem. Soc.*, **1965**, 1685-1692.
24. Miller, B.; Gesner, B. *Tetrahedron Letters*, **1965**, 38, 3351-3354.
25. Collet, A. *Tetrahedron*, **1987**, *43* (24), 5725-5759.
26. Vickery, E.; Pahler, L.; Eisenbraun, E. *J. Org. Chem.*, **1979**, *44* (24), 4444-4446.
27. Patai, S. *The Chemistry of the Ether Linkage*, Wiley-Interscience, New York, 1967, pp. 445-498.
28. Williamson, C. S. *J. Chem. Soc.*, **1851**, 106, 229.
29. Johnstone, R.; Rose, M. *Tetrahedron*, **1979**, *35*, 2169-2173.
30. Benedict, D.; Bianchi, T.; Cate, L. *Synthesis*, **1979**, 428-429.
31. Menger, M.; Takeshita, M.; Chow, J. *J. Am. Chem. Soc.*, **1981**, *103*, 5938-5939.
32. Van Nostrum, C.; Picken, S.; Schouten, A.; Nolte, R. *J. Am. Chem. Soc.*, **1995**, *117*, 9957-9965.