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University of Nevada, Reno

Triphenylene-Based and Tetra-Substituted Indigo Discotic Liquid Crystals

**A thesis submitted in partial fulfillment
of the requirements for the degree of**

PROFESSIONAL CHEMISTRY, E.G., BACHELOR OF SCIENCE

By

BRIANNA C. RUCH

Benjamin T. King, Ph.D., Thesis Advisor

May, 2012

UNIVERSITY
OF NEVADA
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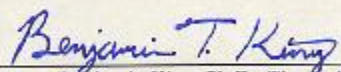
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[May, 2012]

Triphenylene-Based and Tetra-Substituted Indigo Discotic Liquid Crystals

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Abstract

Boron substituted, triphenylene-based discotic liquid crystals (DLCs) were synthesized and assessed for potential usage in organic photovoltaic cells (OPVC). One 3,5 disubstituted discotic was found to have an ideal mesophase ranging from below 30 to almost 200 C. Despite this promise, the triphenylene DLCs' narrow homo-lumo gap of 4.1eV limits OPVC potential. In response, an attempt at synthesizing 3, 3', 4, 4' and 3, 3', 5, 5' tetraalkoxy-substituted indigos was carried out: only the 3, 3', 5, 5' tetramethoxyindigo was successfully synthesized. The synthetic method and characterization of these compounds are provided herein.

Introduction

The rise of silicon-based solar cells in the 1950's has led to an increased demand for more cost-efficient methods of energy harvesting.¹ Organic-based photovoltaic cells (OPVCs), in particular, hold great promise due to their potential low cost of manufacturing and adaptability.² A number of OPVC structures, such as double-layer and mixed bulk heterojunction cells (BHJ), have been researched.² Both cell types consist of electron donating (n-type) and electron accepting (p-type) compounds. While double-layer cells have achieved greater efficiencies to date, their thin-layered construction of acceptor and donor compounds laminated over an electrode allow for minimal contact area between compounds, therein limiting electron flow in these cells.

Bulk heterojunction cells' blend of both acceptor and donor compounds increases the contact area between compounds, thus causing the acceptor/donor interface distance to be less than the exciton diffusion length.³ This means that electrons excited from the donor compound are able to reach the acceptor compound. The ability for electrons to jump between the two compounds lowers the chance of charge recombination.² Although mixed cells have achieved

modest efficiencies,^{4,5} they are subject to a non-uniform mixing of semiconductor types which increases the probability of electron recombination.²

Since mixed cell electron mobility significantly increases with greater degrees of molecular order,⁶ there is research incentive for using discotic liquid crystals (DLCs) as one of the semiconducting materials in OPVCs because of their tendency to self-organize into columns. DLC columnar alignment results from the π - π stacking of polycyclic aromatic cores within the liquid crystal's mesophase.^{4,7} The mesophase's temperature range is dependent upon the peripheral alkyl chains' substitution pattern and length. The addition of alkyl side chains also provides insulation for the aromatic core, causing the conduction of electrons to be more favorable along the columns. This decreases recombination and essentially creates molecular wires.^{4,6}

Triphenylene-based discotic liquid crystals are particularly interesting because they self-organize into hexagonal columnar mesophases (Col_h) homeotropic to the substrate^{4,6} (See Figure

1). Despite there being numerous publications on donor triphenylene based DLC compounds, fewer acceptor compounds are currently in the literature.

Density functional theory (DFT) calculations done by Carey Johnson have proven that the addition of

boron to the periphery of a traditional triphenylene core results in an electron-accepting compound with

electron affinities similar to C_{60} , the current acceptor standard.³ Therefore this research aims to synthesize and evaluate the potential boron substituted DLC compounds have for use in OPVCs.

Figure 3: Indiscriminate stacking of n (pink) and p (blue) type compounds.

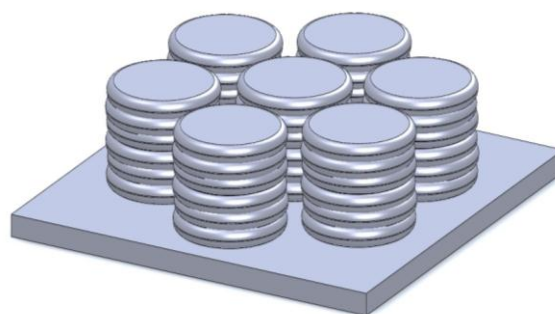


Figure 1: Hexagonal columnar packing forming homeotropic to the substrate.

Ideally the acceptor and donor compounds would interdigitate without stacking on top of each other (See Figure 2). When using triphenylene compounds as both acceptor/donors the compounds have a tendency to stack upon each other indiscriminately (See Figure 3). This stacking is un-favorable because it prevents the flow of electrons from the acceptor molecule to the electrode. For the solar cell to function, an electron donor must be excited by a photon to produce an exciton (electron and hole pair). The electron is then transferred to an acceptor compound, which in turn transmits the charge to the electrode. The movement of the hole in the opposite direction completes the circuit. With the acceptor and donor compounds stacking there is less probability that the electron acceptor is in contact with the electrode. With nowhere to be transmitted, the charge will recombine.^{2,8,9,10}

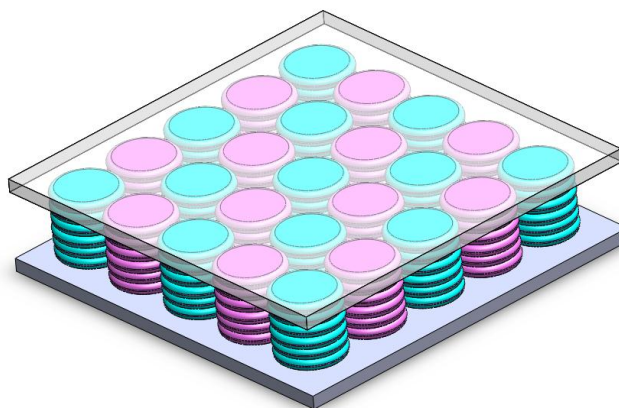


Figure 2: Ideal alignment of p type (blue) and n-type (pink) compounds in a bulk heterojunction cell.



Figure 3: Indiscriminate stacking of n (pink) and p (blue) type compounds.

King *et al.* has proposed that the introduction of dissimilar shaped compounds into a mixed BHJ cell will cause the interdigitation of acceptor/donor columns and prevent the non-uniform mixing of semiconductor types. The increased contact area between donor and acceptor compounds should allow for higher solar cell efficiency due to the increased molecular order.^{8,9}

In addition to triphenylene-based DLCs, the use of indigo as a DLC base will also be examined. Indigo presents an attractive option due to its chromophoric nature, high stability and

propensity for columnar alignment. Currently there has only been one literature attempt at non-polymeric, indigo-based DLCs using a reductive condensation of isatins with 2,3,4-tridodecyloxyphenyl substituents at the 5,5' or 6,6' positions.¹¹ We find it of interest to attempt synthesis of 3, 3', 4, 4' and 3, 3', 5, 5' tetra-substituted indigos with alkyl chains directly attached to the indigo core through the Harley-Mason Method.¹²

Experimental

All synthesis unless otherwise noted were performed under a nitrogen atmosphere.

Instruments used: Varian Ft-nmr 400 Spectrometer, Perkin-Elmer Nicolet 6700 IR, Waters Mass Spec and Differential Scanning Calorimeter (DSC).

2,3,6,7,10,11-hexahydroxytriphenylene (HHTP): A solution of hexamethyloxytriphenylene (HMTP) (9.89 g, 23.75 mmol) in hydrobromic acid (HBr) (300 ml) and acetic acid (AcOH) (300 ml) was refluxed overnight. The resulting crystals were filtered and washed with Et₂O. The product was purified by recrystallization in H₂O/AcOH (3:2). This resulted in 6.52g (83% yield) of grey to clear crystals. Spectra matched previous literature reports.¹³

Bromoresorcinol: 1-Bromo-3,5-dimethoxybenzene (1.0 g, 4.6 mmol) was refluxed overnight in HBr (30 ml) and acetic acid (30 ml). The product was then extracted in ethanol (Et₂O) and hexane, washed with brine and dried in vacuo. This resulted in 0.74 g (85% yield) of product. Spectra matched the literature reports.¹⁴

p-hexyloxybromobenzene.^{15, 16} Hexylbromide (3.89 g, 1 eq), 4-bromophenol (4.0 g, 1 eq), and K₂CO₃ (6.36 g, 2 eq) in DMF (240 ml) were refluxed for three hours. The solution was then extracted in ether, dried over MgSO₄ and the solvent removed. Due to the difficulties of DMF removal, the product was dissolved in hexane and extracted 4 times with HCl (0.5 M) and hexane. Drying in vacuo resulted in a yellow liquid (4.65 g, 78.6% yield). ¹H NMR (CDCl₃) δ:

0.90 (m, 3H), 1.33 (m, 4H), 1.44 (q, $J=8$ Hz, 2H), 1.76 (q, $J=7.2$ Hz, 2H), 3.91 (t, $J=6.8$ Hz, 2H), 6.77 (dt, $J_1=5.6$ Hz, $J_2=3.2$ Hz, 2H), 7.352 (dt, $J_1=5.6$ Hz, $J_2=3.2$ Hz, 2H); [IR ν_{\max} (film): 2928m, 2857m, 1591m, 1488s, 1285m, 1240s, 1169m, 1071m, 818s cm^{-1} . GCMS (EI, M^+) found 256.]

p-octyldecyloxybromobenzene:^{16,17} This product was prepared using the same synthetic method as *p*-hexyloxybromobenzene. ^1H NMR (CDCl_3) δ : 0.87 (t, $J=6.8$ Hz, 3H), 1.25-1.40 (m, 12H), 1.40-1.47 (m, 2 H), 1.76 (qnt, $J=8$ Hz, 2H), 3.91 (t, $J=6.8$ Hz, 2H), 6.77 (d, $J=8.8$ Hz, 2H), 7.36 (d, $J=8.8$ Hz, 2H).

3, 5-di(2-ethylhexyl)bromobenzene: Bromoresorcinol (1.5 g, 1 eq), 1-bromo-2-ethylhexane (3.12 ml, 2.2 eq), and K_2CO_3 (3.31 g, 3 eq) in DMF (40 ml) were refluxed overnight. The solution was then run through a column in hexane and Et_2O (20:1). Removal of solvent gave 1.80 g (54% yield) of product. ^1H NMR (CDCl_3 , 400 MHz) δ = 0.90 (t, $J=7.2$ Hz, 6 H), 0.92 (t, $J=7.2$ Hz, 6 H), 1.27-1.35 (m, 10 H), 1.35-1.56 (m, 8 H), 1.69 (spt, $J=2$ Hz, 2 H), 3.78 (dd, $J_1=5.6$ Hz, $J_2=9.1$ Hz, 2 H), 3.80 (dd, $J_1=5.6$ Hz, $J_2=9.1$ Hz, 2 H), 6.35 (t, $J=2.2$ Hz, 1 H), 6.62 (d, $J=2.2$ Hz, 2 H) ppm; [^{13}C NMR (CDCl_3 , 100 MHz) δ = 161.0, 122.7, 110.1, 100.5, 70.7, 39.3, 30.5, 29.0, 23.8, 26.0, 14.0, 11.1 ppm. HRMS (APPI, M^+) $\text{C}_{22}\text{H}_{37}\text{BrO}_2$ calc 412.1977, found 412.1858.]

4-hexyloxybenzene boronic acid:¹⁷ *p*-hexyloxybromophenol (3.23 g, 1 eq) was dissolved in degassed THF (20 ml) and then cooled to -78°C . BuLi (11.0 ml, 1.4 eq) was added drop wise and the solution allowed stir for 0.5 hours. In a separate schlenk flask a solution of $\text{B}(\text{OiPr})_3$ (4.72 g, 2 eq) in degassed THF was cooled to -78°C . The BuLi solution was then added drop wise to the $\text{B}(\text{OiPr})_3$ flask over a period of 0.5 hrs and the resulting solution allowed to warm to room temperature overnight.

Acetic acid (0.5 ml) in water (1 ml) was added directly to the reaction flask and let stir for 0.5 hours; the solution was filtered and the solvent removed in vacuo. The resulting orange solid was agitated in hexane and then filtered, resulting in a white product (0.9 g, 38% yield). By NMR it was determined the solid was 10:1 product to reactant. Due to difficulties in purification the boronic acid compounds were often used without characterization beyond TLC. Luke Tatum later characterized these compounds using their MIDA derivatives.

p-decyloxybenzene boronic acid: Identical synthesis as provided for 4-hexyloxybenzene boronic acid. Later characterized by Luke Tatum.

3, 5-(2-ethylhexyl) boronic acid: 3,5-(2-ethylhexyl)bromophenol (1.28 g, 1 eq) was dissolved in THF (35 ml) and then cooled to -78°C . BuLi (3.6 ml, 1.4 eq) was added drop wise and the solution allowed to stir for 0.5 hours. In a separate schlenk flask a solution of $\text{B}(\text{O}i\text{Pr})_3$ (1.94 g, 2.5 eq) in THF was cooled to -78°C . The BuLi solution was then added drop wise to the $\text{B}(\text{O}i\text{Pr})_3$ flask and the resulting solution allowed to warm to room temperature overnight.

The solution was then poured over chilled 3 M HCl and allowed to stir for one hour. Purification consisted of running the compound through a column in hexane and EtOH (20:1) and then put on the kugelrohr for one hour at 160°C . The final product was isolated at 1.17 g (69.0% yield). Due to the difficulties in purification, many boronic acids were carried on to the discotic synthesis without purification. Luke undertook characterization of this compound using the MIDA derivatives.

p-hexyloxy discotic: 4-hexyloxyphenyl boronic acid (0.79 g, 3.1 eq) and HHTP (0.38 g, 1 eq) were refluxed in acetonitrile (20 ml) for 24 hours. The discotic precipitated out of solution as a grey powder. This compound was found to decompose from grey to pink in both air and light, so storage under nitrogen in a dark space was necessary. The product was purified in boiling

acetonitrile, filtered and placed under nitrogen. ^1H NMR (taken under nitrogen, CDCl_3 , VT 50°C) δ : 0.94 (m, 9H), 1.38 (m, 12H), 1.50 (m, 6H), 1.83 (q, $J=6.8$ Hz, 6H), 3.99 (t, $J=6.4$ Hz, 6H), 6.97 (d, $J=8.8$ Hz, 6H), 8.01 (d, $J=8.8$ Hz, 6H), 8.16 (s, 6H); ^{13}C NMR (CDCl_3 , VT 50°C) δ : 162.7, 148.3, 136.9, 125.4, 114.4, 105.3, 67.9, 31.6, 29.2, 25.7, 22.5, 13.9 ppm. [IR ν_{max} (film): 2913m, 2850m, 1757s, 1593m, 1601m, 1219s, 1177m, 998s, 859s, 816s, 622s cm^{-1} . HRMS (APPI, M^+) $\text{C}_{54}\text{H}_{57}\text{B}_3\text{O}_9$ calc 882.4277 found 882.4117.]

p-octadecyloxy discotic: Same synthetic procedure as *p*-hexyloxy discotic. ^1H NMR (CDCl_3) δ : 0.88 (t, $J=3.6$, 3H), 1.27 (broad, 32H), 4.03 (t, $J=6.4$ Hz, 2H), 7.02 (d, $J=7.6$ Hz, 6H), 8.08 (d, $J=7.6$ Hz, 6H), 8.31 (s, 6H); ^{13}C NMR (CDCl_3 VT 50°C): 162.8, 148.4, 136.9, 125.5, 114.4, 105.4, 67.9, 31.8, 29.6, 29.6, 29.5, 29.4, 29.2, 29.2, 26.0, 22.6, 13.9 ppm; IR ν_{max} (film): 3503m, 3441m, 2911s, 2845s, 1606s, 1354s, 1606s, 1354s, 1236s, 1148s, 827s cm^{-1} . [HRMS (APPI, M^+) $\text{C}_{90}\text{H}_{129}\text{B}_3\text{O}_9$ calc 1387.9900 found 1387.9525.]

3,5 bis-(2-ethylhexyl) discotic: 3,5 di-(2-ethylhexyl)boronic acid (0.77 g, 3.1 eq) and HHTP (0.22 g, 1 eq) were refluxed in acetonitrile (50 ml) for 24 hours. The discotic precipitates out of solution as a black/brown tar. The tar was dried in vacuo. Purification consisted of dissolving the discotic in chloroform, running it through a plug of celite and precipitating it back out by the drop wise addition of acetonitrile. While this discotic was noticeably less reactive in the presence of light and air than compared with the *p*-discotics, extended exposure did cause a color change from brown to blue/purple. The final product was isolated to give 0.56 g (61.9% yield). ^1H NMR (CDCl_3) δ : 0.92 (m, 36H), 1.34-1.26 (m, 24H), 1.56-1.36 (m, 24H), 1.72 (q, $J=6.4$ Hz, 6H), 3.88 (dd, $J_1=5.2$, $J_2=1.6$ Hz, 12H), 6.65 (t, $J=2.4$ Hz, 3H), 7.28 (d, $J=2.4$ Hz, 6H), 8.33 (s, 6H); [^{13}C NMR (CDCl_3 , 100 MHz) δ = 163.0, 148.4, 137.0, 125.5, 114.4, 105.5, 70.4, 39.3, 30.5, 29.1, 23.8, 23.1, 14.1, 11.1 ppm. IR ν_{max} (film): 2958m, 2926m, 2857m, 1584m, 1426m, 1352s, 1236s,

1157s, 1052m, 891m, 831m, 692m cm^{-1} . HRMS (APPI, M^+) $\text{C}_{84}\text{H}_{117}\text{B}_3\text{O}_{12}$ calc 1350.8811 found 389.2594.]

3, 4-di(2-ethylhexyl)oxybenzaldehyde:¹⁸ 3,4-dihydroxybenzaldehyde (7.2 mmol), 2-ethylhexylbromide (13.5 mmol, 2.2 eq) and finely ground potassium carbonate (3.08 g, 3.1 eq) were dissolved in DMF (20 ml). The solution was placed under nitrogen, fitted with a reflux condenser and the mixture was heated to 55^o C accompanied by stirring for 14 hours. The reaction was then let cool, extracted with ethyl acetate and water, washed with brine, and dried with sodium sulfate. The solution was filtered and the solvent removed under reduced pressure, resulting in a light brown solid (yield 94%). ¹H NMR (CDCl_3) δ : 0.84 (m, 12H), 1.25 (m, 12H), 1.74 (m, 4H, J=6 Hz), 3.38 (q, 2H, J=2.8 Hz), 3.95 (d, 4H, J=5.2 Hz), 6.88 (t, 1H, J=8 Hz), 7.33 (m, 1H), 7.37 (d, 1H, J=2 Hz), 9.76 (s, 1H). IR ν_{max} (film): 2957m, 2923m, 2855, 1680s, 1582, 1505s, 1454s, 1272s, 1123s, 1011 cm^{-1}

3, 4-didecyloxybenzaldehyde: Same synthetic method as 3,4-di(2-ethylhexyl)oxybenzaldehyde. ¹H NMR (CDCl_3) δ : 0.81 (t, 6H, J=7.2 Hz), 1.20 (broad, 24H), 1.39 (m, 4H), 1.79 (m, 4H, J=7.2 Hz), 4.00 (dt, 4H, J₁=6.8, J₂=11.2 Hz), 6.87 (d, 1H, J=8 Hz), 7.32 (dd, 1H, J₁=1.6, J₂=4.8), 7.36 (d, 1H, J=2), 9.76 (s, 1H). IR ν_{max} (film): 2960m, 2924m, 2851, 1713, 1513s, 1462, 1334, 1268s, 1214, 1057 cm^{-1}

3, 4-di(2-ethylhexyloxy)-6-nitrobenzaldehyde:¹⁹ Under nitrogen, nitric acid (70%, 8 mmol) was cooled to 0^oC and a 3,4-dialkyoxybenzaldehyde (0.65 mmol) was added with stirring. The reaction was brought to room temperature over one hour and the solution was poured over ice-water (~25 ml). Due to the alkyl side chains, the product did not precipitate as in the literature; therefore the product was extracted in toluene and run through a silica column of toluene: hexane (20:1). The resulting bright yellow solid was collected in yield of 24%. ¹H NMR (CDCl_3)

δ : 0.83 (m, 12H), 1.25 (m, 12H), 1.72 (m, 4H, $J=6$ Hz), 3.38 (q, 4H, $J=2.8$ Hz), 3.93 (dd, 2H, $J_1=1.6$, $J_2=5.6$ Hz), 7.19 (s, 1H), 7.50 (s, 1H), 10.36 (s, 1H). IR ν_{\max} (film): 2957m, 2924m, 2855, 1688, 1516s, 1458, 1327, 1283s, 1221, 1057, 725s cm^{-1}

3, 4-didecyloxy-6-nitrobenzaldehyde: Same synthetic procedure as 3,4-di(2-ethylhexyloxy)-6-nitrobenzaldehyde, resulting in 50% yield. ^1H NMR (CDCl_3) δ : 0.85 (t, 6H, $J=6.8$ Hz), 1.27 (broad, 24H), 1.48 (m, 4H), 1.85 (m, 4H, $J=6.8$ Hz), 4.13 (t, 4H, $J=6.4$ Hz), 7.38 (s, 1H), 7.58 (s, 1H), 10.43 (s, 1H). IR ν_{\max} (film): 2946, 2909s, 2847s, 1673m, 1564m, 1513s, 1345m, 1272s, 1214s, 1068 cm^{-1}

3, 5-dimethyloxy-6-nitrobenzaldehyde: Same synthetic procedure as 3,4-di(2-ethylhexyloxy)-6-nitrobenzaldehyde except the product was extracted by water and dichloromethane to give light brown crystals. ^1H NMR (CDCl_3) δ : 3.85 (s, 3H), 3.87 (s, 3H), 6.70 (d, 1H, $J=2.8$ Hz), 6.89 (d, 1H, $J=2.8$ Hz), 9.85 (s, 1H).

5, 5', 6, 6'-tetra(2-ethylhexyloxy)indigo: Method A²⁰: The corresponding nitrobenzaldehyde (2.45 mmol) was dissolved in acetone (10 ml), diluted with water (20 ml) and 2 N NaOH (2.5 ml) solution was added and the mixture left stir for five minutes. Because the nitrobenzaldehyde was poorly soluble in acetone and water, after five minutes (and no perceivable indigo) THF was added and the reaction let run for a half hour. No indigo resulted, confirmed by ^1H NMR and IR.

3, 3', 5, 5'-tetramethoxyindigo: Method A was used as seen in the 5, 5', 6, 6'-tetra(2-ethylhexyl)oxyindigo synthesis above. This resulted in dark blue solid precipitate that was filtered, and washed with water and ethanol.

5, 5', 6, 6'-tetradecyloxyindigo (attempt): This compound was attempted using two synthetic methods, both of which failed to produce indigo. *Method B*²⁰: The corresponding nitrobenzaldehyde (2.16 mmol) and nitromethane (2.59 mmol) in methanol were treated at 0^o C

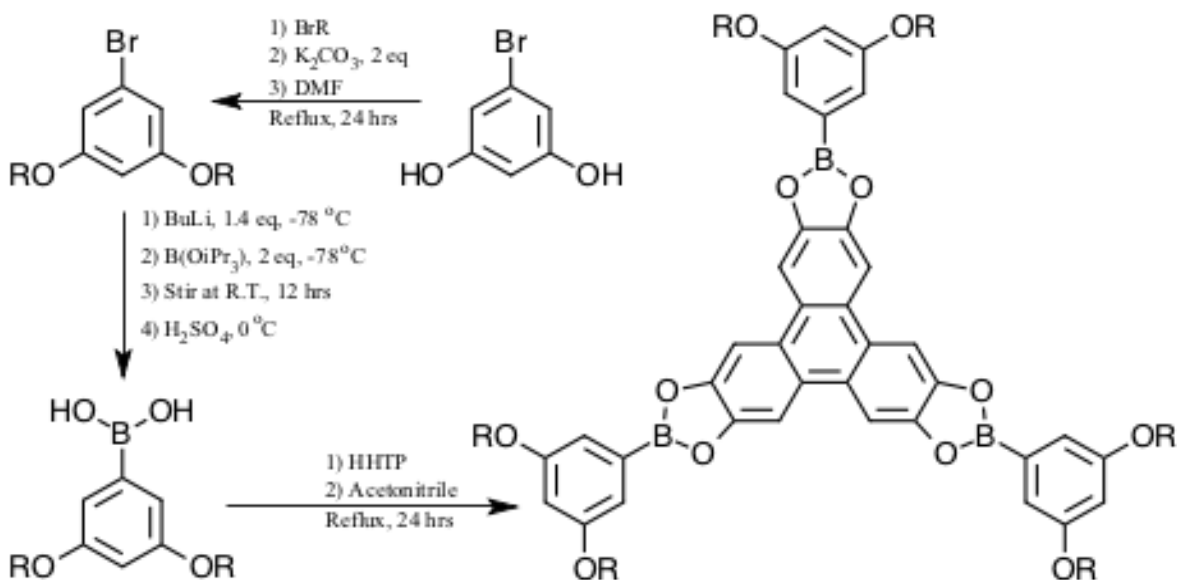
with a solution of sodium methoxide in methanol (4 ml of 0.9 g Na in 10 ml MeOH). Because of the additional side chains, THF was added to the solution until the nitrobenzaldehyde dissolved. After stirring overnight on ice, a yellow solid was collected washed with ether and re-dissolved in water and THF. 2 N NaOH (3 ml) was added to the solution, followed by the slow addition with stirring of sodium dithionite (1.5 g). Air was drawn through the solution for two hours. Gave brown solid which showed starting material in addition to numerous other side products by TLC, ^1H NMR and IR. IR ν_{max} (film): 3427(broad), 2917s, 2847s, 1640m, 1516s, 1458, 1349, 1276s, 1203s, 1035s cm^{-1} *Harvey-Manson Method*.¹² Under nitrogen, 3,4-didecyloxy-6-nitrobenzaldehyde (1.98 g) was dissolved in acetone (5 ml) and 10% sodium hydroxide solution (5 drops) was added. The solution was let stir and after 1 hr water (30 ml) and more 10% sodium hydroxide solution (5 ml) was added. The solution was let sit overnight. Gave clay red solid with some starting material still present confirmed by ^1H NMR and IR. No perceivable indigo was formed. IR ν_{max} (film): 3408, 2913s, 2851s, 1702, 1513s, 1458m, 1330m, 1272s, 1210m, 1068s cm^{-1}

Results and Discussion

Triphenylene-Based DLCs

Two substitution patterns of triphenylene-based DLCs were synthesized. The overall synthetic methods for both the para and 3,5 substituted discotics are highly similar; the para discotic synthesis is summarized in Scheme 1. The versatility and high yield of this synthetic method is ideal for usage in OPVCs.

Scheme 1: Synthetic route to the 3,5 substituted discotics.



Differential Scanning Calorimetry (DSC)

All triphenylene discotics were run through a DSC by Luke Tatum to establish whether the discotics were liquid crystalline in nature. A liquid crystal will have an additional phase between the solid and liquid transitions called the mesophase. For the purpose of using the synthesized discotics in photovoltaic devices it would be optimal for the discotic liquid crystals to have a large mesophase that extends below and above room temperature.

The p-hexyloxy discotic showed only one transition; therein confirming it was not a liquid crystalline molecule. Indeed all p-substituted discotics synthesized were either not liquid crystalline or their mesophases were found at temperatures exceeding temperatures greater than 100°C.

This prompted the synthesis of the 3,5 substituted discotics since the peripheral alkyl chains have been shown to influence the phase-transition temperatures from crystalline to liquid crystalline.¹ Of the discotics synthesized, only the 3,5-di(3,7-dimethyloctyloxy) discotic was found to have a promising mesophase from below 30 to almost 200°C. Despite there being only

one main transition in the DSC (See Figure 4) liquid crystalinty was confirmed by POM; the first transition is not visible due to temperature limitations of the DSC. The temperature range of the 3,5-di(3,7-dimethyloctyloxy) discotic's mesophase is believed to be, in part, caused by the presence of multiple diastereomers.

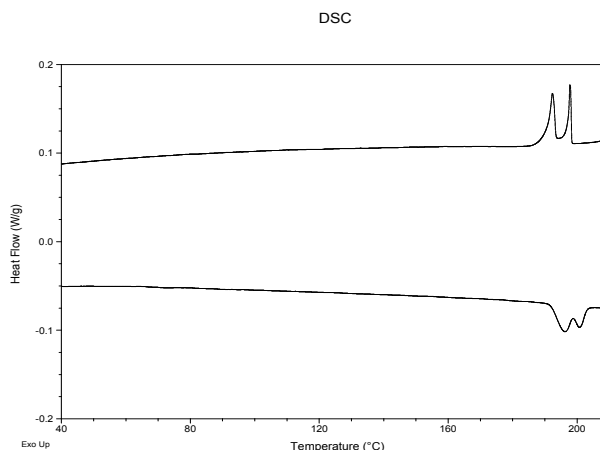


Figure 4: DSC of the 3,5-di(3,7-dimethyloctyloxy) discotic.

Density Functional Theory Calculations (DFT)

DFT calculations were performed by Carey Johnson to show the addition of boron to the triphenylene periphery lowers the energy of the lowest unoccupied molecular orbital (LUMO) by around 1eV. Calculations at the B3LY/6-31G* level of theory gave a LUMO of -1.23 eV, and a HOMO-LUMO gap of 4.11 eV. In comparison to the original triphenylene core, the overall HOMO-LUMO gap remained unchanged. Therefore, while the addition of boron to the triphenylene periphery does decrease the LUMO energy, a band gap of 4.11 eV is still highly limited in its absorption possibilities. Ideally, we would prefer band gaps of around 1.1eV to 2eV.⁸

UV-Vis

The UV-Vis of the 3,5-di(3,7-dimethyloctyloxy) discotic (See Figure 5) further confirms the DFT calculations. Note the only absorption is ~275nm; this coincides with a HOMO-LUMO band gap

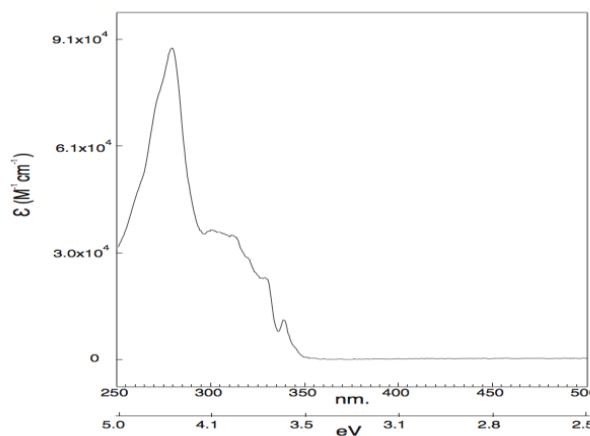


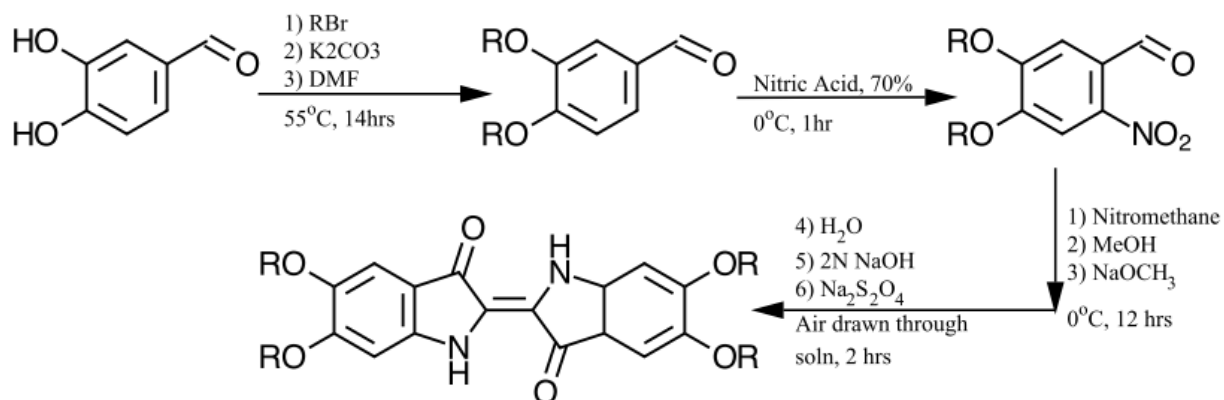
Figure 5: UV-Vis spectra of the 3,5-di(3,7-dimethyloctyloxy) discotic

of 4.51eV. This absorption differs from the DFT calculated value (4.11 eV) by less than 10%. Because the molecule absorbs only in the ultraviolet region its' potential in OPVCs is highly constrained.

Indigo-Based DLCs

Three synthetic methods and two substitution patterns of indigo-based DLCs were attempted. All methods proved ineffectual for synthesizing a 3,4,3',4' alkyloxy-substituted indigo. While there have been literature reports of the 3, 4, 3', 4' tetramethoxy compound, it has not been synthesized on large scale, nor has a yield greater than 4% been reported.^{12, 20, 21} Despite the poor literature yield, our original interest was to synthesize the compound with longer alkyl groups (decyl, 2ethylhexyl, and 3, 7 dimethyloctyloxy) to test for liquid crystalline properties. While the methods varied in concentrations (Method A²¹ is most divergent) the main overall synthesis can be seen in Scheme 2. The synthetic route was proven by characterization to be valid until the cyclization step. Due to the addition of the long alkyl chains, the solubility of the dialkyloxy nitrobenzenes in the literature solutions of acetone and water had to be altered (usually an addition of THF). This could have diminished the already low expected yields.

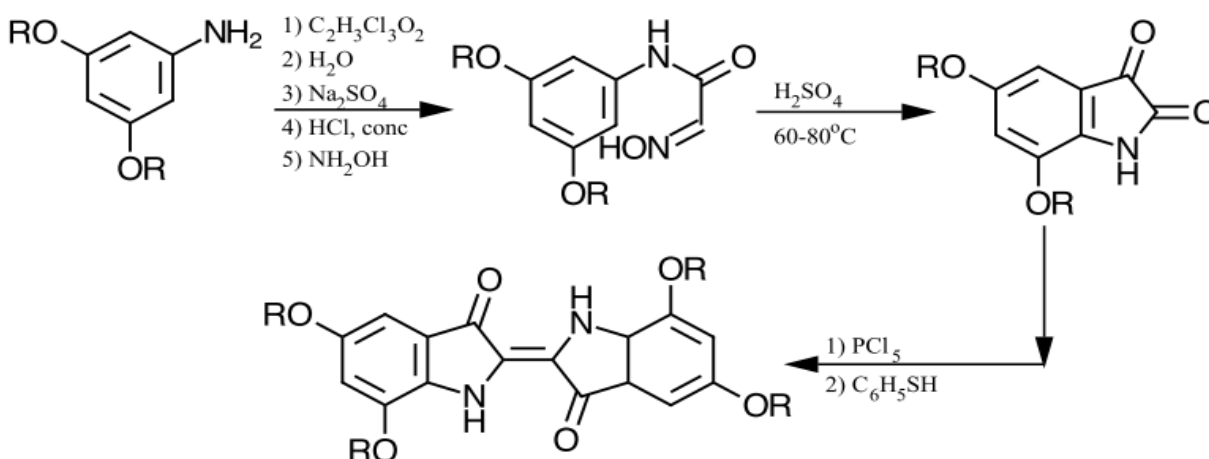
Scheme 2: Synthetic route to the 3, 3', 4, 4' tetra substituted indigo using Method B.



Literature reports show that the substitution to the indigo core drastically affects the cyclization yield; for the 3' monosubstituted 23% yield, the 4' monosubstituted yield 70%.¹¹ Due to the failure of the 3,4,3',4' alkyloxy-substituted indigo synthesis, the 3, 5, 3',5' methoxyindigo(which has a literature yield of 38%)²⁰ was attempted using Method B²¹. This resulted in a dark blue/ purple indigo powder. From here it will be necessary to add longer alkyl groups before cyclization.

Should this method prove invalid, synthesis through the isatin precursor may be another option¹¹. This method was not originally tried because it requires a slightly more intensive synthesis route and the precursors are not as readily available (See Scheme 3).

Scheme 3: Proposed synthetic route using isatin precursors.



Conclusion

Two unique varieties of electron-deficient, triphenylene based DLCs were synthesized and characterized. The syntheses of these compounds have proven replicable on large scale and easily modifiable. One 3,5 substituted discotic was proven to have an ideal mesophase ranging from below 30 to almost $200^\circ C$. Despite this promise, the large and nonadjustable HOMO-LUMO gap prevents the molecule from absorbing visible light; therein significantly decreasing

the potential efficiency of the solar cell. Attempts at tetramethoxy indigo compounds mainly proved ineffectual due to poor yield and solubility.

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Note: I participated in all synthetic procedures specified in the experimental segment of this paper. Some of the spectra used to tabulate data were taken by Luke Tatum and are enclosed by [] in the experimental. The DSC and UV-Vis provided in this paper were taken by Luke Tatum. DFT calculations for the boron periphery were done by Carey Johnson.