# Probing the Structural Features that Influence the Mesomorphic Properties of Substituted Dibenz[a,c]anthracenes

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Probing the Structural Features that Influence the Mesomorphic Properties of Substituted Dibenz[a,c]anthracenes

Joseph A. Paquette, Katie M. Psutka, Colin J. Yardley, and Kenneth E. Maly*

Department of Chemistry and Biochemistry, Wilfrid Laurier University, Waterloo, Ontario N2L 3C5 Canada

*To whom correspondence should be addressed. E-mail: kmaly@wlu.ca
Abstract

We report the synthesis and mesophase characterization of a series of novel hexaalkoxydibenzanthracenes in order to probe the effect of side-chain length variation and substituents on the mesophase temperature range. A series of hexaalkoxydibenzo[a,c]anthracenes (2a-i) with varying chain lengths were prepared by Suzuki coupling of the appropriate boronate ester with the corresponding dialkoxy-dibromonaphthalenes, followed by oxidative cyclization. Compounds 2a-i were also brominated in the 10 and 13-positions to yield the corresponding dibromo series 4a-i. While none of the compounds 2a-i exhibited columnar mesophases, all of the compounds in series 4a-i did exhibit columnar phases over broad temperature ranges. To further investigate the effect of substituents on the mesomorphic properties of hexaalkoxydibenzanthracenes, we also prepared iodo-substituted 8, nitro-substituted 9, and amino-substituted 10. A comparison of the mesophase temperature range with previously reported compounds 3-7 shows that electron-withdrawing groups promote the formation of stable mesophases. However, our results also suggest that the substituents affect mesophase stability by participating in intermolecular contacts within the columnar stacks of the mesophase.

Keywords: liquid crystals, aromatic compounds, self-assembly, pi-pi interactions, synthesis
Introduction

Columnar liquid crystalline phases are formed from disc-shaped compounds that typically feature a polycyclic aromatic core with several peripheral flexible side chains.\textsuperscript{1-3} In the columnar liquid crystal phase (mesophase), these compounds form $\pi$-stacked arrays that allow them to transport charge along the columnar axis. Because of their charge transport properties, these materials show promise as organic semiconductors that can be used in applications such as photovoltaic solar cells, organic light emitting diodes, and field effect transistors.\textsuperscript{4-6} A key requirement for the use of these materials as organic semiconductors is the ability to tune the liquid crystal phase range to suit the desired application. Therefore, understanding how molecular structure influences the mesomorphic properties is critically important for the design of these materials.

Columnar mesophases arise in part from a microsegregation of the aromatic cores, which promote crystalline order, from the side chains, which are liquid-like and flexible.\textsuperscript{1} As such, the nature and length of the side chains are very important factors in determining the mesophase temperature range. However, given that columnar mesophases have significant $\pi$-$\pi$ stacking within the columns, noncovalent interactions such as $\pi$-stacking are thought to play an important role in mesophase formation and in determining the stability of the mesophase. Consequently, the structure and size of the aromatic core are important determining factors in controlling the mesophase temperature range, with larger aromatic cores often showing broad mesophase ranges with high clearing temperatures.\textsuperscript{7-12} The introduction of substituents onto the aromatic core can impact the extent of $\pi$-stacking interactions and therefore be used to tune mesophase stability.\textsuperscript{13-15}
Hexaalkoxytriphenylenes such as 1 are among the most widely studied columnar liquid crystalline materials, although they typically exhibit columnar mesophases over relatively narrow temperature ranges above room temperatures.\textsuperscript{16-18} Alkoxy-substituted dibenz[a,c]anthracenes (e.g. 2-7), where the PAH core is extended as compared to the corresponding triphenylenes, have until recently received relatively little attention as potential columnar liquid crystalline materials.\textsuperscript{11,19-21} Williams and coworkers were the first to report an example of a dibenzanthracene derivative (3) exhibiting a columnar hexagonal mesophase.\textsuperscript{11} The mesophase range of 3 was much broader than that of the corresponding triphenylene, suggesting that extending the aromatic core stabilizes the mesophase through improved $\pi$-stacking interactions. More recently, we reported the synthesis and mesophase characterization of a series of related hexa(decyloxy)dibenz[a,c]anthracenes (2, 4-7).\textsuperscript{19} Surprisingly, the parent hexa(decyloxy)dibenz[a,c]anthracene 2 did not exhibit any columnar liquid crystalline phase, while compounds 3-7, bearing substituents in the 10- and/or 13-positions all exhibited columnar mesophases over broad temperature ranges. Based on this limited set of dibenzanthracene derivatives, electron-withdrawing substituents in these positions appear to promote the formation stable mesophases over broad temperature ranges. These results are consistent with other reports that show electron withdrawing substituents attached to the disc-shaped core lead to the formation of mesophases over broad temperature ranges.\textsuperscript{13,15} Together, these studies support the idea that electron-withdrawing groups pull electron density away from the aromatic core and thereby favour $\pi$-stacking.\textsuperscript{13,22,23}
However, the absence of a mesophase for the parent compound 2 as compared with 3, which bears electron-donating methyl groups suggests that other factors are influencing the mesophase behaviour, and that substituents are not simply exerting an electronic effect, which has also been noted with triphenylene derivatives.\textsuperscript{24} To further explore how structural features influence liquid crystalline properties in this class of compounds, we report an expanded study that examines the effect of chain length variation on mesophase temperature range of dibenzanthracenes 2a-i and their brominated derivatives 4a-i. We have also prepared an expanded set of dibenzanthracenes 8-10 bearing substituents at the 10- and 10- and 13-positions to probe understand the effect of substituents on the aromatic core on columnar liquid crystalline properties.
Results and Discussion

Synthesis

We previously reported the synthesis of hexa(decyloxy)dibenz[a,c]anthracene 2 using an approach involving a Suzuki-Miyaura cross-coupling of a substituted naphthalene and an alkoxy-substituted aryl boronate, followed by an oxidative cyclization.\textsuperscript{19} We also demonstrated that electrophilic bromination introduced substituents in the 10- and 13-positions. By careful control of the stoichiometry of bromine added, either the monobromo- derivative 6 or the dibromo- derivative 4 could be formed. Here we employed a similar approach to prepare a series of hexaalkoxydibenz[a,c]anthracenes and their dibromo-substituted derivatives where the alkoxy chain lengths were varied from hexyl to decyl chains. It is noteworthy that with this modular approach we can independently vary the side chains on the anthracene moiety and the fused benzene rings, allowing us to produce a set of nine compounds from the three different chains lengths.

The appropriate 2,3-dialkoxy-6,7-dibromonaphthalene\textsuperscript{19,25,26} (11a-c) and dialkoxyphenyl boronate ester (12a-c)\textsuperscript{19} underwent Suzuki cross-coupling to yield compounds 13a-i (Scheme 1). While the Suzuki couplings gave the desired diaryl naphthalenes in moderate to good yields, purification of these compounds proved challenging: in many cases side-products reaction remained after column chromatography and these relatively low-melting solids were difficult to purify by recrystallization. Therefore, these compounds were used without further purification in the subsequent oxidative cyclizations. The oxidative ring closing furnished the desired
hexaalkoxydibenzanthracenes (2a-i), which were readily purified by column chromatography and recrystallization. Bromination using Br$_2$ in CHCl$_3$ yielded the corresponding dibromo derivatives 4a-i.

Given that the introduction of bromo substituents in the 10- and 13- positions proceeded well, we decided to use electrophilic aromatic substitutions to introduce other substituents onto the hexadecyloxydibenzanthracene 2i in order to probe the effects of these substituents on mesomorphic properties. Unfortunately, efforts to prepare the
corresponding mono- and diiodo-substituted dibenzanthracene derivatives 8 and 14 using standard iodination conditions of iodine in periodic acid in glacial acetic acid were unsuccessful, leading instead to oxidation of 2i to give the corresponding dibenzanthracenequinone 15 (Scheme 2). To circumvent this problem, the monoiodo derivative 8 was prepared in 51% yield by lithium-halogen exchange of compound 6 and subsequent trapping with iodine.

**Scheme 2.**

Direct nitration of 2 was also unsuccessful, possibly because of the limited solubility of the starting material in the reaction conditions. We therefore carried out nitration on the dibromo-didecyloxynaphthalene (11c) to give compound 16 in 55% yield, which was then subjected to Suzuki cross-coupling with the aryl boronate 12c to furnish 17 in 59% yield (Scheme 3). Subsequent oxidative cyclization yielded the desired nitro-substituted compound 9 in 91% yield. The nitro compound 9 could be used to access the corresponding amino derivative (10). After attempting several different standard reduction methods for converting aromatic nitro compounds to the corresponding
anilines, we found that sodium borohydride in the presence of nickel chloride hexahydrate in THF/methanol furnished 12 in a modest 24% yield.\textsuperscript{27}

Scheme 3.

\emph{Mesomorphic properties – Effect of side chain variation}

The mesomorphic properties of compounds 2a-i and 4a-i were evaluated by polarized optical microscopy and differential scanning calorimetry. The phase transition temperatures of these compounds are summarized in Figure 1. None of the parent hexaalkoxydibenzanthracene derivatives 2a-i exhibited columnar mesophases, instead showing transitions directly from the crystalline solid to isotropic liquid. The melting points of 2a-i range from approximately 60-90 °C, with those compounds with longer alkoxy chains having lower melting points. The distinct absence of any columnar
mesophases for series \(2a-i\) is surprising, especially since all of the corresponding triphenylene derivatives (1) exhibit columnar hexagonal phases.\(^{28,29}\) The reasons for these differences are not clear, but may be the result of differences in effective packing: in the columnar phase, the triphenylenes can pack effectively in a columnar stack, while the slightly elongated dibenzanthracenes do not pack as well in the columns.

Similarly, hexaalkoxydibenzophenazines, which are structurally very similar to the dibenzanthracenes, exhibit columnar mesophases over broad temperature ranges. The difference in mesomorphic behaviour between the dibenzanthracenes and the corresponding dibenzophenazines may be attributed to differences in the propensity of these compounds to engage in \(\pi\)-stacking interactions. The electron-deficient heteroaromatic dibenzophenazine is more likely to form \(\pi\)-stacks than the electron-rich dibenzanthracene.\(^{19,30}\)
Figure 1. Summary of phase transition temperatures for compounds series 2a-i and 4a-i
Determined by DSC on 2\textsuperscript{nd} heating. The glass-mesophase transitions were not always clearly observed by DSC, so polarized optical microscopy was used in these cases.

In contrast to the hexaalkoxydibenzanthracene series 2a-i, all of the dibromo-substituted compounds 4a-i exhibit columnar mesophases over broad temperature ranges (Figure 1). Polarized optical microscopy of compounds 4a-i showed dendritic textures with homeotropically aligned domains consistent with uniaxial columnar hexagonal phases (Figure 2). Variable-temperature powder X-ray diffraction studies on a representative compound in this series supports the phase assignment as a columnar hexagonal mesophase.\textsuperscript{19} It is noteworthy that most of the compounds in series 4 do not crystallize
on cooling from the columnar mesophase but instead form glasses that preserve the order of the columnar mesophase. In some cases these glass transitions could be distinguished by DSC, while in other cases they were determined by polarized optical microscopy as the point at which the textures no longer changes upon shearing or compression.
Figure 2. Representative polarized optical micrographs of a) 4b b) 4g and c) 4e taken upon cooling near the isotropic liquid-columnar mesophase transition.
The stability of the mesophase is reflected by the clearing point (the transition between the liquid crystal phase and isotropic liquid phase), with a higher clearing point corresponding to a more stable mesophase. As such, even though the melting transition is not clearly observed because of the formation of a glassy phase, the mesophase characteristics in this series of compounds can be compared by considering the clearing points, which are clearly observable by polarized optical microscopy and differential scanning calorimetry. A comparison of the clearing points of compounds 4a (R=\(R'\)=C6), 4e (R=\(R'\)=C8), and 4i (R=\(R'\)=C10) reveals that shorter side chains lead to increased clearing points.

When the side chains on the benzo-fused rings is R=C\(_{10}\)H\(_{21}\), changing the R' side chains adjacent to the bromo substituents from hexyl to decyl has only a small effect on the clearing point. In contrast, when R=C\(_{6}\)H\(_{13}\), changing the R' substituent has a more dramatic effect on the clearing point, with shorter R' chains leading to higher clearing points. Thus the effect of the R and R' side chains on the mesophase range are interrelated. The interdependence of both side chains on the fused benzene rings and the anthracene moieties may be due to overall changes in molecular shape from more more disk-shaped to elliptical. For example, compound 2c, bearing hexyloxy chains on the fused benzo groups and decyloxy chains on the anthracene end, has the lowest clearing point and is also the compound with the most elongated, elliptical shape.

Overall, the observation of columnar mesophases over broad temperature ranges for series 4a-i while series 2a-i shows no mesomorphic behaviour suggests that the bromo substituents in the 10- and 13-positions of 4a-i are important for the formation of
columnar mesophases in these systems and lead to the formation of very stable mesophases. A possible explanation for the induction of stable mesophases upon bromination is that the bromine atoms increase the surface area of the core of the molecule, thereby increasing Van der Waals interactions in the columnar stacks. The increased intermolecular contacts involving the bromo substituents would also be expected in the solid state, and should give rise to an increase in the melting transition temperature. However, as already noted, compounds 4a-i have mesophases extending to relatively low temperatures and generally do not solidify upon cooling; instead, they exhibit glassy states at low temperature. This behaviour can be attributed to the bromo groups influencing the conformational distribution of the adjacent alkoxy side chains. In 4a-i, these side chains are not coplanar with the aromatic ring, which may prevent effective packing in the crystalline solid.

In order to further probe the effect of substituents on the aromatic core on mesomorphic properties, we examined the effect varying substituents in the 10 or 10-and 13 positions of the hexaalkoxydibenzanthracenes while maintaining a constant side chain length. Specifically, we compared the mesomorphic behaviour of compounds 3-7, which had been previously reported, to compounds 8-10, which were prepared in this study.

All of the compounds bearing substituents in the 10 or 10 and 13 positions exhibited columnar mesophases as shown by DSC and polarized optical microscopy (Table 1). Furthermore, polarized optical microscopy studies (Figure 2) as well as variable-temperature powder XRD on a subset of these compounds show that these compounds form columnar hexagonal mesophases.
Table 1. Summary of phase transition temperatures of 4-10.

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<th>Compound</th>
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<td>&lt;sup&gt;4&lt;/sup&gt;&lt;sup&gt;19&lt;/sup&gt;</td>
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<tr>
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<td>Cr 51 Col 193 I</td>
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<td>X = I, Y = H</td>
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<td>10</td>
<td>X = NH&lt;sub&gt;2&lt;/sub&gt;, Y = H</td>
<td>Cr 34 Col 86 I</td>
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<sup>a</sup>Phase transition temperatures are reported by DSC upon heating at 5 °C/min and are reproducible over three heating and cooling cycles.
Figure 3. Representative polarized optical micrographs of compounds a) 8, b) 9, and c) 10 near the isotropic-columnar phase transition, upon cooling.
Several studies have suggested that electron-withdrawing substituents attached to the aromatic core of a discotic mesogen lead to broad mesophase temperature ranges with increased clearing points.\textsuperscript{13-15,32,33} For example, Bushby and coworkers showed that the addition of substituents onto the core of a hexaalkoxytriphenylene significantly influences the mesophase temperature range (18a-f).\textsuperscript{14,15,32} Specifically, strongly electron-withdrawing substituents such as nitro and fluoro groups lead to higher clearing transition temperatures, while electron-donating methyl or amino groups showed significant lowering of the clearing point or even a disappearance of the mesophase. Similarly, Williams and coworkers demonstrated that the mesophase stability as estimated from the clearing transition temperature showed a good correlation with Hammett sigma values in a series of substituted dibenzophenazines (19a-f). For compounds 19e-g, bearing electron-withdrawing groups, no mesophase was observed.\textsuperscript{13}

The higher clearing points associated with stabilization of the mesophase can be attributed to more favorable \( \pi \)-stacking interactions.\textsuperscript{13} In electron-rich aromatic systems such as alkoxy-substituted triphenylenes, \( \pi \)-stacking interactions are electrostatically

\begin{center}
\includegraphics[width=\textwidth]{chemical_structures.png}
\end{center}
disfavoured between two electron-rich aromatic systems. The addition of electron-withdrawing substituents reduces the electron density of the aromatic ring consequently the repulsive interactions are minimized, thereby stabilizing the mesophase.\textsuperscript{13,22,23} It is noteworthy that in many of these systems the electron-withdrawing groups also introduce a dipole moment, so the mesophase may be further stabilized by dipole-dipole interactions.

To probe the potential electronic effects of substituents on the mesophase temperature in our hexaalkoxydibenzanthracenes, we made a similar comparison of clearing transition temperatures with Hammett parameters. The plot of clearing point versus Hammett $\sigma_p$ for both the monosubstituted series and disubstituted series shows a strong correlation ($R^2=0.95$) (Figure 4), consistent with previous findings that suggest that electron-withdrawing substituents stabilize the mesophase.
Figure 4. Clearing transition temperature vs. Hammett $\sigma_p$ values. The red circles correspond to the monosubstituted series (6, 7, 8, 9, 10), while the blue triangles correspond to the disubstituted series (3, 4, 5). For disubstituted compounds 3-5, the Hammett $\sigma_p$ values were doubled to account for the two substituents.

However, the absence of any columnar mesophase for the parent hexaalkoxydibenzanthracene 2 is a notable exception to this trend. The absence of a mesophase for 2 even though compounds 3 and 10 (which are more electron-rich) do exhibit columnar mesophases, suggests that the substituents on the dibenzanthracene core are not stabilizing the mesophase purely by electronic effects. This behaviour is in contrast with the corresponding hexaalkoxytriphenylenes, where compounds 18e and 18f,
bearing amino and methyl groups, respectively, do not exhibit mesophases, while the 
parent hexaalkoxytriphenylene does. We propose that the compounds bearing 
substituents in the 10- and 10- and 13-positions are able to pack more effectively in the 
columnar mesophase with more extensive intermolecular contacts. In other words, the 
parent dibenzanthracene 2, with its elongated polycyclic core, could stack into columns 
but would leave void spaces due to inefficient packing. By placing substituents on the 
core, the core becomes more disk-shaped and can pack more effectively by involving the 
substituents in the intermolecular contacts within the columnar stacks.

Support for the proposed increased surface for intermolecular stacking 
interactions with substituents is provided by the comparison of compounds 2a-i and their 
dibrominated derivatives 4a-i (Figure 1). While none of compounds 2a-i exhibit 
columnar mesophases, all of compounds 4a-i exhibit columnar mesophases with high 
clearing points, in most cases close to 100 °C higher than the melting points of 2a-i. It is 
plausible that the observed differences between these two series are the result of 
improved intermolecular interactions within the columns as opposed to an electronic 
effect of relatively weakly electron-withdrawing bromo substituents.

Conclusions

In summary, we have prepared a series of hexaalkoxydibenzanthracenes with 
varying alkoxy side chains and their bromo- derivatives. The 
hexaalkoxydibenzanthracenes do not exhibit columnar mesophases, regardless of the 
side-chain lengths. In contrast, the bromo-substituted derivatives all exhibit columnar 
mesophases over broad temperatures ranges. We have also prepared a series of
hexaalkoxydibenzanthracene derivatives where the substituents on the core are varied in order to probe the effect of substituents on the mesophase temperature range. Our results suggest that electronic effects of substituents on the core influence the mesophase range, with electron-withdrawing substituents stabilizing the mesophase. However, our results also indicate that the substituent effects on mesophase range are also influenced by other factors. Specifically, we propose that substituents are able to participate in intermolecular contacts within the columns, effectively increasing the size of the core and promoting the formation of extended π-stacked arrays.

Experimental

Synthesis

$^1$H-NMR and $^{13}$C-NMR were recorded using a Varian 300 MHz Unity Inova NMR Spectrometer, using indicated deuterated solvents purchased from CIL Inc. All chemicals used were purchased from Sigma-Aldrich and were used as received. 1-pinacolatoboron-3,4-bis(alkyloxy)benzenes 12a-c$^{19}$ and 2,3-dibromo-6,7-dialkoxy napthalenes (11a-c)$^{19,25,26}$ were prepared according to literature procedures. Compounds 2i, 4i, 5, 6, and 7 were reported previously.$^{19}$ Anhydrous and oxygen-free solvents were dispensed from a custom-built solvent purification system which used purification columns packed with activated alumina and supported copper catalyst (Glasscontour, Irvine, CA). Oven or flame-dried glassware was used for all reactions. Melting points were determined by DSC at a heating rate of 5 °C per minute and are reported from the peak of the phase transition. High resolution MALDI mass spectra
were recorded at the Centre Régional de Spectrométrie de Masse à l’Université de Montréal using an Agilent LC-MSD TOF spectrometer.

**General procedure for the synthesis of 1,2-dialkoxy-5,6-bis(3,4-dialkoxybenzene)naphthalene (13):** Pd(OAc)$_2$ (5 %) and PPh$_3$ (10 %) were dissolved in 20 mL degassed toluene, followed by the addition of 2,3-dibromo-6,7-bis(decyloxy)naphthalene (1 eq) and 1-pinacolatoboron-3,4-bis(decyloxy)benzene (2.09 eq.). To the reaction mixture 7 mL degassed aq. 2.0 M K$_3$PO$_4$ (excess) was added. The mixture was heated to 80°C and left to stir for 48 hours. The reaction mixture was cooled to room temperature, followed by the addition of 20 mL dichloromethane and washed with H$_2$O (2x20 mL) and brine (1x20 mL). The organic layer was dried with MgSO$_4$ and solvent removed under reduced pressure to give product. The crude product was further purified using column chromatography with hexanes/dichloromethane (60:40) unless otherwise stated. Due to difficulties with purification, compound series 13 was used without further purification.

**General Procedure for the synthesis of hexaalkoxydibenzo[a,c]anthracenes (2a-i):** 2,3-bis[3,4-dialkoxyphenyl]-6,7-dialkoxyanthracene (1 eq.) was dissolved in 20 mL dry CH$_2$Cl$_2$. FeCl$_3$ (6 eq) was added to the solution and stirred for 1 hour. The solution was poured into MeOH (100 mL) and the resulting precipitate was collected by suction filtration. The crude product was purified by a short silica column eluting with CH$_2$Cl$_2$ and the solvent was removed via rotary evaporator, followed by recrystallization in acetone.
2,3,6,7,11,12-hexakis(hexyloxy)dibenz[a,c]anthracene (2a): 2,3-bis[3,4-dihexyloxybenzene]-6,7-bis(hexyloxy)naphthalene (0.214 g, 0.243 mmol) and FeCl₃ (0.241 g, 1.48 mmol) were used. Yielded a light brown solid (0.136 g, 64 %). m.p. 89 °C. ¹H NMR (300 MHz, CDCl₃): δ 8.70 (s, 2H), 8.11 (s, 2H), 7.81 (s, 2H), 7.33 (s, 2H), 4.31-4.18 (m, 12H), 2.00-1.93 (m, 12H), 1.61-1.55 (m, 12H), 1.47-1.39 (m, 24H), 0.98-0.92 (18H). ¹³C NMR (75 MHz, CDCl₃): δ 150.08, 149.50, 149.28, 128.31, 126.71, 124.28, 124.14, 119.57, 107.93, 107.70, 107.02, 70.02, 69.63, 69.07, 31.93, 31.87, 29.68, 29.65, 29.33, 26.11, 26.08, 22.92, 22.89, 14.32, 14.30. HRMS (MALDI) calc’d for C₅₈H₈₆O₆ m/z 878.6424, found 878.6419.

2,3,6,7-tetrakis(hexyloxy)-11,12-bis(octyloxy)dibenz[a,c]anthracene (2b): 2,3-bis[3,4-dihexyloxyphenyl]-6,7-dioctyloxyphenanthrene (0.20 g , 0.214 mmol) and FeCl₃ (0.212g, 1.304 mmol) were used to obtain a light brown solid (0.19 g, 94.9 % yield). m.p. 87 °C. ¹H NMR (300 MHz, CDCl₃): δ 8.71 (s, 2H), 8.12 (s, 2H), 7.81 (s, 2H), 7.33 (s, 2H), 4.32-4.18 (m, 12H), 2.00-1.93 (m, 12H), 1.62-1.55 (m, 12H), 1.43-1.32 (m, 32H), 0.98-0.91 (m, 18H). ¹³C NMR (75 MHz, CDCl₃): δ 149.41, 148.83, 148.60, 127.63, 126.02, 123.60, 123.47, 118.86, 107.05, 106.36, 69.34, 68.96, 68.39, 31.39, 31.23, 28.95, 28.84, 28.67, 25.68, 25.38, 25.01, 22.20, 13.65, 13.59. HRMS (MALDI) calc’d for C₆₂H₉₄O₆ m/z 934.7050, found 934.7033.

2,3,6,7-tetrakis(hexyloxy)-11,12-bis(decyloxy)dibenz[a,c]anthracene (2c): 2,3-bis[3,4-dihexyloxyphenyl]-6,7-didecyloxyphenanthrene (0.75 g , 0.75 mmol) and FeCl₃ (0.737 g, 4.53 mmol) were used to obtain a light brown product (0.70 g, 94 % yield). m.p. 83 °C. ¹H NMR (300 MHz, CDCl₃): δ 8.70 (s, 2H), 8.11 (s, 2H), 7.80 (s, 2H), 7.32 (s, 2H), 4.31-4.17 (m, 12H), 1.97-1.92 (m, 12H), 1.61-1.56 (m, 12H), 1.42-1.38 (m, 40H), 0.97-0.91
(m, 18H). 13C NMR (75 MHz, CDCl3): δ 150.10, 149.52, 149.29, 128.32, 126.71, 124.29, 124.16, 119.56, 107.97, 107.05, 70.03, 69.64, 69.08, 32.16, 31.93, 31.16, 29.90, 29.84, 29.71, 29.67, 29.65, 29.61, 29.38, 26.38, 26.10, 26.08, 25.00, 22.93, 22.91, 22.90, 14.35, 14.31, 14.29. HRMS (MALDI) calc’d for C66H102O6 m/z 990.7676, found 990.7685.

2,3,6,7-tetrakis(octyloxy)-11,12-bis(hexyloxy)dibenz[a,c]anthracene (2d): 2,3-bis[3,4-dioctyloxyphenyl]-6,7-dihexyloxynaphthalene (0.20 g, 0.201 mmol) and FeCl3 (0.19 g, 1.23 mmol) to give a light brown solid (0.15 g, 75.3 % yield). m.p. 86 °C. 1H (300 MHz, CDCl3): δ 8.68 (s, 2H), 8.10 (s, 2H), 7.80 (s, 2H), 7.32 (s, 2H), 4.31-4.18 (m, 12H), 2.00-1.93 (m, 12H), 1.61-1.57 (m, 12H), 1.43-1.33 (m, 40H), 0.97-0.89 (m, 18H). 13C NMR (75 MHz, CDCl3): δ 150.11, 149.55, 149.31, 128.33, 126.72, 124.32, 124.19, 119.55, 108.02, 107.83, 107.08, 70.06, 69.69, 69.08, 32.11, 31.88, 29.74, 29.58, 29.36, 26.45, 26.44, 26.06, 22.94, 22.88, 14.35, 14.27. HRMS (MALDI) calc’d for C66H102O6 m/z 990.7676, found 990.7685.

2,3,6,7,11,12-hexakis(octyloxy)dibenz[a,c]anthracene (2e): 2,3-bis[3,4-dioctyloxyphenyl]-6,7-dioctyloxynaphthalene (0.574 g, 0.547 mmol) and FeCl3 (0.541 g, 3.340 mmol) were used to give a light brown solid (0.521 g, 90.9 % yield). m.p. 74 °C. 1H (300 MHz, CDCl3): δ 8.69 (s, 2H), 8.11 (s, 2H), 7.80 (s, 2H), 7.32 (s, 2H), 4.30-4.18 (m, 12H), 1.97-1.92 (m, 12H), 1.60-1.57 (m, 12H), 1.42-1.32 (m, 48H), 0.92-0.88 (m, 18H). 13C NMR (75 MHz, CDCl3): δ 150.10, 149.52, 149.30, 128.32, 126.71, 142.30, 124.17, 119.56, 107.77, 107.05, 70.05, 69.67, 69.09, 32.16, 32.10, 29.90, 29.84, 29.73, 29.71, 29.61, 29.58, 29.34, 26.44, 26.39, 25.01, 25.00, 22.93, 14.35. HRMS (MALDI) calc’d for C70H110O6 m/z 1046.8302, found 1046.8297.
2,3,6,7-tetrakis(octyloxy)-11,12-bis(decyloxy)dibenz[a,c]anthracene (2f): 2,3-bis[3,4-dioctyloxyphenyl]-6,7-didecyloxynaphthalene (0.648 g, 0.586 mmol) and FeCl₃ (0.580 g, 3.57 mmol) were used to get a pale brown solid (0.208 g, 32.2 % yield). m.p. 74 °C. 

1H NMR (300 MHz, CDCl₃): δ 8.69 (s, 2H), 8.11 (s, 2H), 7.80 (s, 2H), 7.32 (s, 2H), 4.30-4.17 (m, 12H), 1.99-1.92 (m, 12H), 1.54-1.58 (m, 12H), 1.42-1.29 (m, 56H), 0.92-0.87 (m, 18H) 

13C NMR (75 MHz, CDCl₃): δ 150.10, 149.53, 149.30, 128.33, 126.72, 124.30, 124.17, 119.57, 107.98, 107.77, 107.06, 70.05, 69.68, 69.09, 32.17, 32.11, 29.91, 29.85, 29.73, 29.72, 29.61, 29.58, 29.39, 26.44, 26.39, 25.00, 22.94, 14.36. HRMS (MALDI) calc’d for C₇₄H₁₁₈O₆ m/z 1102.8928, found 1102.8924.

2,3,6,7-tetrakis(decyloxy)-11,12-bis(hexyloxy)dibenz[a,c]anthracene (2g): 2,3-bis[3,4-didecyloxyphenyl]-6,7-dihexyloxynaphthalene (0.90 g, 0.91 mmol) and FeCl₃ (0.88 g, 5.44 mmol) were used to obtain a light brown solid (0.85 g, 84.6 % yield). m.p. 63 °C. 

1H NMR (300 MHz, CDCl₃): δ 8.69 (s, 2H), 8.10 (s, 2H), 7.80 (s, 2H), 7.32 (s, 2H), 4.30-4.18 (m, 12H), 1.99-1.92 (m, 12H), 1.63-1.55 (m, 12H), 1.45-1.29 (m, 56H), 0.97-0.87 (m, 18H) 

13C NMR (75 MHz, CDCl₃): δ 150.12, 149.55, 149.32, 128.33, 126.72, 124.32, 124.19, 119.56, 108.04, 107.84, 107.09, 70.07, 69.69, 69.08, 32.16, 31.87, 29.93, 29.86, 29.78, 29.76, 29.61, 29.35, 26.44, 26.05, 22.93, 22.87, 14.33, 14.27. HRMS (MALDI) calc’d for C₇₄H₁₁₈O₆ m/z 1102.8928, found 1102.8923.

2,3,6,7-tetrakis(decyloxy)-11,12-bis(octyloxy)dibenz[a,c]anthracene (2h): 2,3-bis[3,4-didecyloxyphenyl]-6,7-dioctyloxynaphthalene (0.06 g, 0.052 mmol) and FeCl₃ (0.051 g, 0.315 mmol) were used to give a light brown solid (0.033 g, 55.1 % yield). m.p. 64 °C. 

1H NMR (300 MHz, CDCl₃): δ 8.70 (s, 2H), 8.11 (s, 2H), 7.80 (s, 2H), 7.32 (s, 2H), 4.28-4.20 (m, 12H), 1.97-1.94 (m, 12H), 1.59-1.55 (m, 12H), 1.36-1.25 (m, 64H),
2,3,6,7,11,12-hexakis(decyloxy)dibenz[a,c]anthracene (2i). 2,3-bis[3,4-didecyloxyphenyl]-6,7-didecyloxyanthracene (1.214 g, 1.00 mmol) was dissolved in 20 mL dry CH₂Cl₂. FeCl₃ (0.97 g, 6.00 mmol) was added to the solution and stirred for 1 hour. Yielded a light yellow solid (1.11 g, 91.4%). m.p. 60 °C. ¹H NMR (300 MHz, CDCl₃): δ 8.69 (s, 2H), 8.10 (s, 2H), 7.80 (s, 2H), 7.32 (s, 2H), 4.28-4.20 (m, 12H), 1.97-1.95 (m, 12H), 1.59-1.55 (m, 12H), 1.43-1.28 (m, 72H), 0.91-0.87 (m, 18H). ¹³C NMR (75 MHz, CDCl₃): δ 150.08, 149.50, 149.28, 128.31, 126.71, 124.29, 124.16, 119.55, 107.96, 107.74, 107.04, 70.03, 69.65, 69.07, 32.17, 29.94, 29.91, 29.87, 29.85, 29.79, 29.77, 29.72, 29.63, 29.39, 26.45, 26.39, 22.94, 14.35. HRMS (MALDI) calc’d for C₈₂H₁₃₄O₆ m/z 1215.0180, found 1215.0175.

General Procedure for dibromination of 2: The appropriate hexaalkoxydibenzanthracene 2 (1 eq.) was dissolved in 50 mL chloroform. Bromine (2.3 equivalents) was added dropwise to the solution and the mixture was left to stir for 1 hour. The reaction mixture was washed with sodium thiosulfate, water then brine. The organic layer was dried with MgSO₄, filtered then dried. The crude product was purified using column chromatography, Hexanes/dichloromethane (50:50). The product was then recrystallized in acetone to yield a light brown solid.

10,13-dibromo-2,3,6,7,11,12-hexakis(hexyloxy)dibenz[a,c]anthracene (4a): 2,3,6,7,11,12-hexakis(hexyloxy)dibenz[a,c]anthracene (0.067 g, 0.076 mmol) and Br₂
(0.028 g, 0.175 mmol) were used to yield a white solid (92 %) $^1$H (300 MHz, CDCl$_3$): δ 9.19 (s, 2H), 8.13 (s, 2H), 7.77 (s, 2H), 4.33-4.17 (m, 12H), 2.01-1.91 (m, 12H), 1.65-1.55 (m, 12H), 1.43-1.39 (m, 24H), 0.97-0.95 (m, 18H). $^{13}$C NMR (75 MHz, CDCl$_3$): δ 150.42, 149.99, 149.39, 128.99, 129.09, 124.93, 123.34, 121.22, 116.17, 108.34, 107.59, 74.80, 69.90, 69.74, 31.96, 31.93, 30.55, 29.64, 29.61, 26.12, 26.08, 26.04, 22.93, 22.91, 22.90, 14.31, 14.28. HRMS (MALDI) calc’d for C$_{58}$H$_{84}$Br$_2$O$_6$+H m/z 878.6424, found 878.6419.

10,13-dibromo-2,3,6,7-tetrakis(hexyloxy)-11,12-bis(octyloxy)dibenz[a,c]anthracene (4b): 2,3,6,7-tetrakis(hexyloxy)-11,12-bis(octyloxy)dibenz[a,c]anthracene (0.010 g, 0.106 mmol) and Br$_2$ (0.0374 g, 0.234 mmol) were used to obtain a light brown solid (0.082 g, 70.4 % yield). $^1$H (300 MHz, CDCl$_3$): δ 9.22 (s, 2H), 8.15 (s, 2H), 7.78 (s, 2H), 4.33-4.17 (m, 12H), 2.01-1.91 (m, 12H), 1.62-1.55 (m, 12H), 1.44-1.33 (m, 32H), 0.97-0.91 (m, 18H). $^{13}$C NMR (75 MHz, CDCl$_3$): 150.44, 150.00, 149.41, 129.01, 128.12, 124.95, 123.36, 121.26, 116.19, 108.41, 107.61, 74.81, 69.91, 69.77, 32.11, 31.95, 31.92, 30.59, 29.74, 29.62, 29.59, 29.57, 26.39, 26.11, 26.08, 22.92, 22.90, 14.35, 14.31, 14.28. HRMS (MALDI) calc’d for C$_{62}$H$_{92}$Br$_2$O$_6$+H m/z 1090.5261, found 1090.5220.

10,13-dibromo-2,3,6,7-tetrakis(hexyloxy)-11,12-bis(decyloxy)dibenz[a,c]anthracene (4c): 2,3,6,7-tetrakis(hexyloxy)-11,12-bis(decyloxy)dibenz[a,c]anthracene (0.07 g, 0.0705 mmol) and Br$_2$ (0.0248 g, 0.150 mmol) were used to obtain a light brown solid (0.071 g, 87.6 % yield). $^1$H NMR (300 MHz, CDCl$_3$): δ 9.24 (s, 2H), 8.18 (s, 2H), 7.80 (s, 2H), 4.34-4.17 (m, 12H), 2.01-1.91 (m, 12H), 1.65-1.57 (m, 12H), 1.47-1.25 (m, 40H), 0.97-0.87 (m, 18H). $^{13}$C (75 MHz, CDCl$_3$): δ 150.49, 150.03, 149.46, 129.04, 128.15, 124.99, 123.40, 121.28, 116.19, 108.48, 107.65, 74.82, 69.93, 69.84, 32.15, 31.95, 31.91,
10,13-dibromo-2,3,6,7-tetrakis(octyloxy)-11,12-bis(hexyloxy)dibenz[a,c]anthracene (4d): 2,3,6,7-tetrakis(octyloxy)-11,12-bis(hexyloxy)dibenz[a,c]anthracene (0.05 g, 0.05 mmol) and Br₂ (0.018 g, 0.11 mmol) were used to obtain a light brown solid (0.03 g, 52.2 %). ¹H NMR (300 MHz, CDCl₃): δ 9.21 (s, 2H), 8.15 (s, 2H), 7.77 (s, 2H), 4.32-4.17 (m, 12H), 2.00-1.91 (m, 12H), 1.61-1.29 (m, 52H), 0.94-0.89 (m, 18H). ¹³C (75 MHz, CDCl₃): δ 150.4, 150.0, 148.4, 129.0, 128.1, 124.9, 123.3, 121.2, 116.2, 108.4, 107.6, 74.8, 69.9, 69.8, 32.2, 31.9, 31.8, 30.5, 29.93, 29.86, 29.8, 29.7, 29.6, 26.45, 26.43, 26.0, 25.5, 22.9, 22.9, 14.33, 14.3.

10,13-dibromo-2,3,6,7,11,12-hexakis(octyloxy)dibenz[a,c]anthracene (4e): 2,3,6,7,11,12-hexakis(octyloxy)dibenz[a,c]anthracene (0.100 g, 0.095 mmol) and Br₂ (0.035, 0.219 mmol) were used to obtain a white solid (0.11 g, 96.1 % yield). ¹H NMR (300 MHz, CDCl₃): δ 9.12 (s, 2H), 8.07 (s, 2H), 7.72 (s, 2H), 4.31-4.18 (m, 12H), 2.01-1.92 (m, 12H), 1.65-1.57 (m, 12H), 1.43-1.33 (m, 48H), 0.94-0.89 (m, 18H). ¹³C (75 MHz, CDCl₃): δ 149.51, 149.14, 148.49, 128.09, 127.20, 124.05, 122.45, 120.36, 115.38, 107.37, 106.64, 74.011, 69.04, 68.86, 31.35, 29.86, 29.01, 28.94, 28.90, 28.85, 25.70, 25.68, 25.66, 22.17, 13.58. HRMS (MALDI) calc’d for C₇₀H₁₀₈Br₂O₆ m/z 1202.6513, found 1202.6544.

10,13-dibromo-2,3,6,7-tetrakis(octyloxy)-11,12-bis(decyloxy)dibenz[a,c]anthracene (14f): 2,3,6,7-tetrakis(octyloxy)-11,12-bis(decyloxy)dibenz[a,c]anthracene (0.100 g, 0.091 mmol) and Br₂ (0.033 g, 0.208 mmol) were used to obtain a white solid (0.097 g,
H NMR (300 MHz, CDCl$_3$): $\delta$ 9.16 (s, 2H), 8.10 (s, 2H), 7.75 (s, 2H), 4.32-4.17 (m, 12H), 2.01-1.92 (m, 12H), 1.62-1.57 (m, 12H), 1.43-1.30 (m, 56H), 0.93-0.88 (m, 18H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 150.31, 149.93, 149.26, 128.90, 128.00, 124.84, 123.25, 121.15, 116.17, 108.17, 107.44, 74.79, 69.84, 69.66, 32.18, 32.13, 32.12, 30.63, 29.95, 29.90, 29.82, 29.79, 29.77, 29.71, 29.67, 29.63, 29.14, 26.48, 26.46, 26.43, 22.96, 14.36. HRMS (MALDI) calc'd for C$_{74}$H$_{116}$Br$_2$O$_6$ $m/z$ 1258.7139, found 1258.7079.

10,13-dibromo-2,3,6,7-tetrakis(decyloxy)-11,12-bis(hexyloxy)dibenzo[a,c]anthracene (14g): 2,3,6,7-tetrakis(decyloxy)-11,12-bis(hexyloxy)dibenzo[a,c]anthracene (0.100 g, 0.091 mmol) and Br$_2$ (0.033 g, 0.209 mmol) were used to obtain a light brown solid (0.101 g, 88.0 % yield). $^1$H NMR (300 MHz, CDCl$_3$): 9.24 (s, 2H), 8.17 (s, 2H), 7.79 (s, 2H), 4.33-4.17 (m, 12H), 2.01-1.92 (m, 12H), 1.64-1.59 (m, 12H), 1.44-1.29 (m, 56H), 0.93-0.87 (m, 18H). $^{13}$C NMR (75 MHz, CDCl$_3$): 150.46, 150.01, 149.43, 129.03, 128.13, 124.98, 123.38, 121.28, 116.19, 108.48, 107.68, 74.83, 69.94, 69.80, 32.17, 31.95, 30.55, 29.96, 29.94, 29.87, 29.79, 29.69, 29.62, 26.46, 26.43, 26.04, 22.94, 22.91, 14.35, 14.32. HRMS (MALDI) calc’d for C$_{74}$H$_{116}$Br$_2$O$_6$ $m/z$ 1258.7139, found 1258.7156.

10,13-dibromo-2,3,6,7-tetrakis(decyloxy)-11,12-bis(octyloxy)dibenzo[a,c]anthracene (14h): 2,3,6,7-tetrakis(decyloxy)-11,12-bis(octyloxy)dibenzo[a,c]anthracene (0.010 g, 0.0086 mmol) and Br$_2$ (0.0032 g, 0.0198 mmol) were used to obtain a white solid (0.0107 g, 94.0 % yield). $^1$H (300 MHz, CDCl$_3$): $\delta$ 9.24 (s, 2H), 8.18 (s, 2H), 7.79 (s, 2H), 4.33-4.17 (m, 12H), 2.01-1.91 (m, 12H), 1.60-1.55 (m, 12H), 1.43-1.25 (m, 64H), 0.91-0.86 (m, 18H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$ 150.48, 150.03, 149.44, 129.03, 128.15, 124.99,
123.38, 121.29, 116.19, 108.51, 107.68, 74.83, 69.93, 69.81, 32.16, 32.10, 30.57, 29.93, 29.86, 29.77, 29.72, 29.61, 29.55, 26.43, 25.70, 22.92, 14.34. HRMS (MALDI) calc’d for C\textsubscript{76}H\textsubscript{124}Br\textsubscript{2}O\textsubscript{6} m/z 1314.7765, found 1314.7744.

**10,13-dibromo-2,3,6,7,11,12-hexakis(decyloxy)dibenz[a,c]anthracene (4i):**

2,3,6,7,11,12-hexakis(decyloxy)dibenz[a,c]anthracene (0.300 g, 0.247 mmol) and Br\textsubscript{2} (0.029 mL, 0.567 mmol) give a light brown solid. (0.319 g, 94.0 %), \textsuperscript{1}H NMR (300 MHz, CDCl\textsubscript{3}): \(\delta\) 9.25 (s, 2H), 8.18 (s, 2H), 7.79 (s, 2H), 4.32 (t, \(J = 6.60\) 4H), 4.43 (t, \(J = 6.30\)), 4.18 (t, \(J = 6.30\), 4H), 2.00-1.91 (m, 12H), 1.60-1.54 (m, 12H), 1.38-1.26 (m, 72H), 0.90-0.86 (m, 18H). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}): \(\delta\) 150.47, 150.02, 149.43, 129.04, 128.14, 124.98, 123.39, 121.29, 116.20, 108.34, 107.67, 74.83, 69.94, 69.80, 32.17, 30.59, 29.95, 29.93, 29.91, 29.87, 29.78, 29.62, 29.60, 26.43, 26.39, 25.00, 22.94, 14.34. HRMS (MALDI) calc’d for C\textsubscript{82}H\textsubscript{132}Br\textsubscript{2}O\textsubscript{6}+H m/z 1370.8391, found 1370.8385.

**Synthesis of 10-bromo-2,3,6,7,11,12-hexakis(decyloxy)dibenz[a,c]anthracene (6):**

2,3,6,7,11,12-hexakis(decyloxy)dibenz[a,c]anthracene, (0.250 g, 0.206 mmol) was dissolved in 50 mL CHCl\textsubscript{3}. Bromine (0.035 g, 0.216 mmol) was added dropwise to the solution and left to stir for 1 hour. The organic layer was washed with sodium thiosulfate, water then brine. The organic layer was dried with MgSO\textsubscript{4}, filtered and the solvent was removed under reduced pressure. A column was performed on the crude product, Hexanes/DCM (50:50), followed by recrystallization in acetone to yield a pale yellow/brown solid (0.243 g, 91.1 %). \textsuperscript{1}H-NMR (300 MHz, CDCl\textsubscript{3}, 30 mM): \(\delta\) 9.15 (s, 1H), 8.65 (s, 1H), 8.17 (s, 1H), 8.07 (s, 1H), 7.78 (s, 2H), 7.30 (s, 1H), 4.31-4.22 (m, 8H), 4.18-4.16 (m, 4H), 1.98-1.91 (m, 12H), 1.60-1.56 (m, 12H), 1.42-1.29 (m, 84H), 0.91-0.87 (m, 18H). \textsuperscript{13}C NMR (75 MHz, CDCl\textsubscript{3}): \(\delta\) 152.29, 149.98, 149.87, 149.36, 149.26,
147.17, 129.89, 128.14, 127.36, 126.51, 124.73, 124.30, 124.16, 123.48, 120.69, 119.96, 116.28, 108.15, 107.81, 107.70, 106.84, 73.94, 69.99, 69.92, 69.69, 68.93, 32.18, 30.63, 29.96, 29.92, 29.89, 29.81, 29.74, 29.64, 29.53, 26.53, 26.46, 22.95, 14.36.

HRMS (MALDI) calc’d for C$_{82}$H$_{133}$BrO$_6$+H $m/z$ 1292.9286, found 1292.9280.

**Synthesis of 10-cyano-2,3,6,7,11,12-hexakis(decyloxy)dibenz[a,c]anthracene (7):**

10-bromo-2,3,6,7,11,12-hexakis(decyloxy)dibenz[a,c]anthracene (0.10 g, 0.077 mmol) was dissolved in dry DMF (5 mL). CuCN (9.0 mg, 0.10 mmol) was added to the solution. Reaction was fitted with a condenser and heated to reflux for 18 hours while kept under a N$_2$ atmosphere. Solution cooled to room temperature, followed by the addition of 20 mL of water. Ethylenediamine (1 mL) was added to the solution and shaken. Extracted with DCM (3 x 25 mL), washed with water followed by 1 M HCl. Organic layer was dried with MgSO$_4$, filtered and solvent removed under reduced pressure. A brown solid crude product was obtained. Column chromatography was performed hexanes/dichloromethane (50:50), followed by recrystallization in acetone to yield a bright yellow solid (0.042 g, 48%). $^1$H-NMR (300 MHz, CDCl$_3$) : $\delta$ 8.73 (s, 1H), 8.37 (s, 1H), 7.94 (s, 1H), 7.80 (s, 1H), 7.63 (s, 1H), 7.62 (s, 1H), 7.28 (s, 1H), 4.34 (t, $J$ = 6.6 Hz, 2H), 4.30-4.22 (m, 8H), 4.17 (t, $J$ = 6.3 Hz, 2H), 1.96-1.91 (m, 12H), 1.56-1.52 (m, 12H), 1.43-1.26 (m, 72H), 0.93-0.89 (m, 18H). $^{13}$C NMR (75 MHz, CDCl$_3$): $\delta$154.90, 150.62, 150.08, 150.00, 149.44, 149.14, 128.38, 128.35, 128.13, 125.76, 124.57, 124.37, 123.40, 123.04, 120.10, 117.59, 116.11, 112.17, 107.66, 107.52, 107.45, 107.28, 101.80, 75.36, 69.89, 69.72, 69.58, 69.10, 32.21, 32.20, 30.61, 30.01, 29.99, 29.93, 29.89, 29.80, 29.76, 29.68, 29.65, 29.48, 26.52, 26.19, 22.97, 14.37. HRMS (MALDI) calc’d for C$_{83}$H$_{133}$NO$_6$+H $m/z$ 1240.0133, found 1240.0127.
Synthesis of 10-iodo-2,3,6,7,11,12-hexakis(decyloxy)dibenz[a,c]anthracene (8): 10-bromo-2,3,6,7,11,12-hexakis(decyloxy)dibenz[a,c]anthracene 6 (0.247 g, 0.191 mmol) was added to 25 mL dry THF. Solution was placed in an ice bath and cooled to -42 °C. To the cooled solution was added n-BuLi (0.11 mL, 2.10 M, 1.2 eq.) where it was stirred to 30 minutes while maintaining -42 °C. Molecular iodine (0.097 g, 0.382 mmol) was added to solution, then it was allowed to warm to room temperature. Mixture was then treated with saturated sodium thiosulfate (50 mL). The organic layer was removed and further washed with brine (1x50 mL) and H₂O (1x50 mL). It was dried with MgSO₄ and solvent was removed under reduced pressure. Column chromatography was performed with Hexanes/DCM (70:30). The product was recrystallized in acetone to yield a white solid (0.130 g, 50.7%). ¹H-NMR (300 MHz, CDCl₃): δ 9.12 (s, 1H), 8.65 (s, 1H) 8.21 (s, 1H), 8.10 (s, 1H), 7.80 (s, 2H), 7.34 (s, 1H), 4.32-4.15 (m, 12H), 1.95-1.93 (m, 12H), 1.60-1.54 (m, 12H), 1.42-1.29 (m, 72H), 0.91-0.86 (m, 18H). ¹³C-NMR (75 MHz, CDCl₃): δ 151.50, 150.28, 149.99, 149.85, 149.38, 149.29, 129.98, 128.71, 128.08, 127.73, 125.97, 124.74, 124.25, 124.09, 123.44, 120.02, 108.08, 108.03, 107.91, 107.77, 96.18, 73.75, 70.05, 69.94, 69.72, 69.63, 68.89, 53.63, 32.16, 30.65, 29.94, 29.91, 29.86, 29.78, 29.73, 29.62, 29.54, 26.53, 26.48, 26.44, 25.01, 22.93, 14.34.

Synthesis of 10,13-dicyano-2,3,6,7,11,12-hexakis(decyloxy)dibenz[a,c]anthracene (5):¹⁹ 10,13-dibromo-2,3,6,7,11,12-hexakis(decyloxy)dibenz[a,c]anthracene (0.42 g, 0.306 mmol) was dissolved in 10 mL dry DMF. CuCN (69 mg, 0.76 mmol) was added to the solution. Reaction was heated to reflux and stirred for 24 hours under a N₂ atmosphere. The solution was then cooled to room temperature; 10 mL of ethylenediamine was added, followed by 20 mL H₂O. It was then extracted with DCM
(3x20 mL). The organic layer was washed with 1 M HCl (3x50 mL), H₂O (50 mL) and brine (50 mL). Organic layer was dried with MgSO₄, filtered and concentrated under reduced pressure. Column chromatography was performed with hexanes/dichloromethane (60:40), followed by recrystallization in acetone to yield a bright orange solid (0.04 g, 10.3%). ¹H-NMR (300 MHz, CDCl₃): δ 8.63 (s, 2H), 7.71 (s, 2H), 7.58 (s, 2H), 4.44 (t, J = 6.9 Hz, 4H), 4.21 (m, 8H), 1.96 (m, 12H), 1.61 (m, 12H), 1.29 (m, 72H), 0.89 (m, 18H).

Synthesis of 2,3-dibromo-5-nitro-6,7-bis(decyloxy)naphthalene (16): of nitric acid (50 mL) was cooled to 0 °C in an ice bath, where 20 drops of concentration sulfuric acid was added. 2,3-dibromo-6,7-bis(decyloxy)naphthalene (2.00 g, 3.34 mmol) was slowly added to the acidic mixture. Solution was stirred vigorously overnight while allowing the mixture to warm to room temperature overnight (12 hours). The solution was neutralized with saturated NaHCO₃ (50 mL). The product was then extracted with 50 mL EtOAc, followed by a washing with NaHCO₃ (1 x 50 mL), brine (50 mL) and water (50 mL). The organic layer was dried with MgSO₂, filtered and concentrated under reduced pressure. Column chromatography was performed with hexanes/EtOAc (90:10), followed by a recrystallization in EtOH to give a white solid (1.18 g, 54.9 %). ¹H-NMR (300 MHz, CDCl₃): δ 8.01 (s, 1H), 7.87 (s, 1H), 7.10 (s, 1H), 4.21 (t, J = 6.6 Hz, 2H), 4.10 (t, J = 6.3 Hz, 2H), 1.92-1.87 (m, 2H), 1.79-1.75 (m, 2H), 1.29-1.25 (m, 28H), 0.90-
0.86 (m, 6H). $^{13}\text{C-NMR}$ (75 MHz, CDCl$_3$): $\delta$ 152.50, 142.58, 140.90, 130.98, 129.95, 125.64, 123.14, 122.51, 120.22, 108.81, 75.69, 69.61, 32.12, 30.19, 29.81, 29.78, 29.61, 29.55, 29.22, 26.36, 25.92, 22.91, 14.32.

**2,3-bis[3,4-didecyloxyphenyl]-6,7-didecyloxy-5-nitronaphthalene (17):** Charge a flask with 2,3-dibromo-5-nitro-6,7-bis(decyloxy)naphthalene (1.00 g, 1.55 mmol), 1-pinacolatoboron-3,4-bis(decyloxy)benzene (1.67 g, 3.24 mmol), Pd(OAc)$_2$ (0.035, 0.16 mmol) and triphenylphosphine (0.081 g, 0.31 mmol). Added 15 mL of degassed toluene to reagent mixture. Combine organic solution with 7 mL of 2 M K$_3$PO$_4$. Fitted reaction with a condenser, heated to 80 °C and left to stir for 48 hours under a N$_2$ atmosphere. The reaction mixture was cooled to room temperature, added 20 mL of dichloromethane, the organic layer was separated and washed with water then brine. Dried the organic layer with MgSO$_4$, filtered and removed solvent under reduced pressure. Column chromatography was performed in Hexanes/dichloromethane (60:40) and recrystallized in acetone to yield a yellow solid (1.15 g, 58.9 %). $^1\text{H-NMR}$ (300 MHz, CDCl$_3$): $\delta$ 7.74 (s, 1H), 7.60 (s, 1H), 7.27 (s, 1H), 6.79 (s, 4H), 6.63 (s, 1H), 6.59 (s, 1H), 4.23 (t, $J = 6.6$, 2H), 4.14 (t, $J = 6.7$, 2H), 3.97 (t, $J = 6.6$, 4H), 3.70-3.67 (m, 4H), 1.91-1.79 (m, 12H), 1.68-1.64 (m, 4H), 1.49-1.45 (m, 8H), 1.30-1.27 (m, 72H), 0.91-0.87 (m, 18H). $^{13}\text{C-NMR}$ (75 MHz, CDCl$_3$): $\delta$ 151.3, 148.5, 141.9, 141.2, 139.8, 139.5, 133.7, 133.6, 129.4, 119.4, 116.2, 115.8, 75.3, 69.3, 69.2, 31.97, 31.95, 31.93, 30.05, 29.7, 29.68, 29.66, 29.64, 29.60, 29.52, 29.47, 29.43, 29.39, 29.38, 29.36, 29.2, 26.2, 26.11, 26.10, 26.06, 25.8, 22.7, 14.1 HRMS (MALDI) calc’d for C$_{82}$H$_{135}$NO$_8$+H $m/z$ 1262.0188, found 1262.0182.
Synthesis of 10-nitro-2,3,6,7,11,12-hexakis(decyloxy)dibenz[a,c]anthracene (9): 2,3-bis[3,4-didecyloxyphenyl]-6,7-didecyloxy-5-nitronaphthalene (0.500 g, 0.396 mmol) was added to 20 mL dry dichloromethane. FeCl₃ (0.385 g, 2.38 mmol) was added to the solution, placed under a N₂ atmosphere and left to stir for 1 hour. Poured the mixture into MeOH (150 mL) and placed in freezer for 1 hour. Performed a suction filtration to the resulting precipitate, and washed with cold MeOH. A short flash column chromatography was done in dichloromethane to remove the excess FeCl₃ followed by a recrystallization in acetone to yield a yellow solid (0.453 g, 90.7 %). ¹H NMR (300 MHz, CDCl₃): δ 8.48 (s, 1H), 8.37 (s, 1H), 7.91 (s, 1H), 7.74 (s, 1H), 7.63 (s, 1H), 7.61 (s, 1H), 7.25 (s, 1H), 4.27-4.14 (m, 12H), 1.99-1.95 (m, 10H), 1.86-1.81 (m, 2H), 1.59-1.54 (m, 12H), 1.30-1.25 (m, 72H), 0.91-0.86 (m, 18H). ¹³C NMR (75 MHz, CDCl₃): δ 150.78, 150.09, 149.99, 149.36, 149.13, 141.64, 141.60, 128.50, 128.30, 128.07, 124.68, 124.32, 123.29, 122.87, 119.85, 118.29, 114.11, 109.38, 107.60, 107.48, 107.41, 107.15, 75.57, 69.90, 69.63, 69.57, 69.49, 69.25, 32.22, 32.21, 32.19, 30.37, 30.01, 29.95, 29.93, 29.91, 29.88, 29.83, 29.79, 29.76, 29.68, 29.65, 29.51, 26.55, 26.51, 26.10, 22.97, 14.37. HRMS (MALDI) calc’d for C₈₂H₁₃₃NO₈+H m/z 1260.0031, found 1260.0026.

Synthesis of 10-amino-2,3,6,7,11,12-hexakis(decyloxy)dibenz[a,c]anthracene (10): 10-nitro-2,3,6,7,11,12-hexakis(decyloxy)dibenz[a,c]anthracene (0.453 g, 0.359 mmol) and NiCl₂·6H₂O (0.426 g, 1.795 mmol) were dissolved in 20 mL dry THF and 7 mL dry MeOH, solution was orange/green. Added NaBH₄ in small portions to the solutions, where the mixture turned black. Continued stirring for 45 minutes after the addition of base. The crude mixture was filtered and washed with dichloromethane. It was dissolved in 50 mL dichloromethane. The organic layer was washed with water (50 mL) and brine.
(50 mL). The organic layer was dried with MgSO₄, filtered and solvent was removed under reduced pressure. Column chromatography was performed in hexanes/dichloromethane (60:40 → 40:60), followed by a recrystallization in acetone to give a light brown solid (0.108 g, 24.4 %). ¹H-NMR (300 MHz, CDCl₃): δ 8.72 (s, 1H), 8.66 (s, 1H), 8.11 (s, 1H), 8.08 (s, 1H), 7.78 (s, 2H), 6.91 (s, 1H), 4.48 (bs, 2H), 4.29-4.21 (m, 8H), 4.17 (t, J = 6.6 Hz, 2H), 4.11 (t, J = 6.6 Hz, 2H), 1.99-1.85 (m, 12H), 1.59-1.55 (m, 12H), 1.49-1.21 (m, 72H), 0.89 (t, J = 6.6 Hz, 18H). ¹³C NMR (75 MHz, CDCl₃): δ 152.58, 149.69, 149.59, 149.29, 149.26, 134.51, 133.68, 129.95, 127.71, 125.51, 124.46, 124.44, 124.23, 124.03, 120.23, 120.00, 114.51, 108.07, 107.92, 107.85, 107.80, 98.20, 73.43, 69.99, 69.62, 68.39, 32.18, 30.81, 29.95, 29.88, 29.80, 29.72, 29.64, 29.62, 26.58, 26.51, 26.46, 26.44, 22.95, 14.36. HRMS (MALDI) calc’d for C₈₂H₁₃₅NO₆H m/z 1230.0289, found 1230.0284.

**Mesophase Characterization**

Polarized optical microscopy studies were carried out using an Olympus BX-51 polarized optical microscope equipped with a Linkam LTS 350 heating stage and a digital camera. Differential Scanning Calorimetry (DSC) studies were carried out using a TA Instruments DSC Q200 with a scanning rate of 5 °C/min.

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