Sidechain engineering in anthracene derivatives: towards photofunctional liquid crystals

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Abstract: A series of anthracene derivatives were synthesised to explore how their sidechain configurations influenced their phase behaviour and thereby guiding the design of photofunctional liquid crystalline materials. In the case of 9,10-diphenylanthracene derivatives, longer and more alkyl sidechains resulted in lower melting temperatures, yet liquid crystallinity was not observed. A novel room-temperature molecular liquid was synthesised based on 9,10-diphenylanthracene, the optical properties of which may be exploited in photonic applications. Liquid crystallinity was observed in one of the derivatives of 9,10-bis(phenylethynyl)anthracene, forming a nematic phase at around 210°C. These results highlight the potential opportunities for photofunctional materials with enhanced properties if liquid crystalline anthracenes can be found with lower phase transition temperatures.

Keywords: liquid crystal; 9,10-diphenylanthracene; DPA; 9,10-bis(phenylethynyl)anthracene; BPEA; molecular liquid; photon upconversion.

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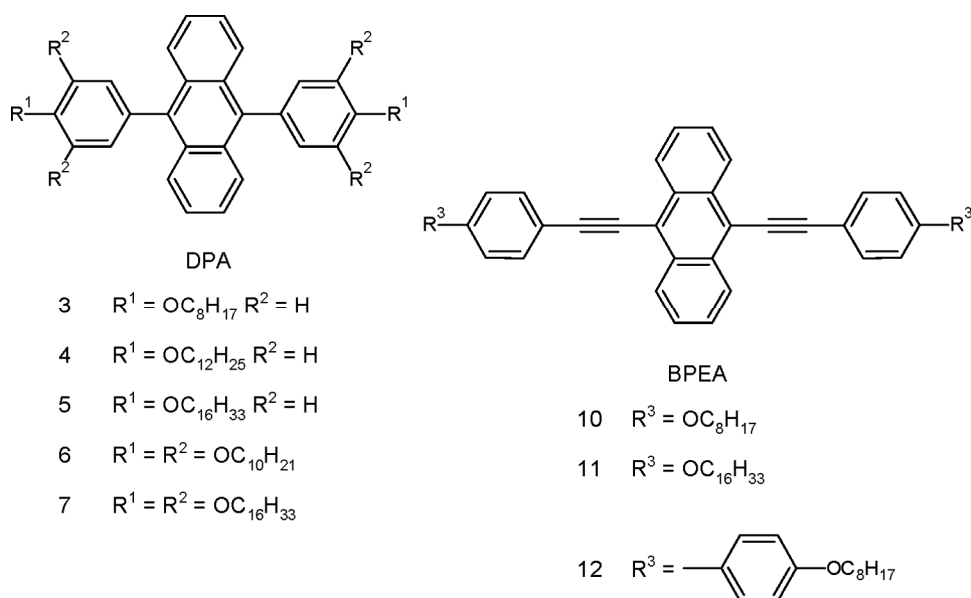# 1 Introduction

Liquid crystalline (LC) materials have the potential to enhance the optoelectronic properties of molecular materials, particularly where long-range order is important. The characteristic order of LC phases is exploited in liquid crystal displays [1–3], and often enhances charge mobilities of π-conjugated materials [4]. Of the functional and synthetically accessible π-conjugated cores that could be augmented with LC properties, 9,10-diphenylanthracene (DPA) and 9,10-bis(phenylethynyl)anthracene (BPEA) (Scheme 1) have received little attention.

The attractive optical properties of DPA and BPEA derivatives include near unit fluorescent quantum yields, which has led to their widespread use in fluorescent labelling [5,6] as well as photon upconversion emitters [7]. Photon upconversion refers to the conversion of multiple (generally two) lower energy photons to a higher energy photon. This process holds promise for next generation of light harvesting coatings for photovoltaic panels [7], provided that it can be achieved in films.

LC anthracenes are attractive components of photon upconverting films, because their order may enhance the long-range excitation energy transfer processes underpinning upconversion. However, there are few existing LC anthracene derivatives. Both dyes (Scheme 1) have a rigid central core, which is a good basis for developing LC materials. However, the two outer phenyl rings in DPA could hinder self-assembly [8,9]. 9,10-Bis{4-(4-pentylcyclohexyl)phenyl}anthracene is the only known LC derivative of DPA [8], forming a smectic A mesophase at 277°C [8]. In contrast, the triple bonds in BPEA allow the outer substituents to freely rotate without altering the electronic properties, which may facilitate self-assembly [10,11]. A few LC derivatives of BPEA are known [10], with LC phases resulting from synthetically demanding asymmetric substitution with different length alkyl sidechains, or where an additional 4-alkyl phenyl group was attached symmetrically [10,11].

Scheme 1　9,10-Diphenylanthracene (DPA) and 9,10-bis(phenylethynyl)anthracene (BPEA) derivatives synthesised

DPA

3	$R^1 = OC_8H_{17}$ $R^2 = H$
4	$R^1 = OC_{12}H_{25}$ $R^2 = H$
5	$R^1 = OC_{16}H_{33}$ $R^2 = H$
6	$R^1 = R^2 = OC_{10}H_{21}$
7	$R^1 = R^2 = OC_{16}H_{33}$

BPEA

| 10 | $R^3 = OC_8H_{17}$ |
| 11 | $R^3 = OC_{16}H_{33}$ |
| 12 | $R^3 =$ ◯—OC_8H_{17} |

The paucity of existing LC anthracenes motivates the synthesis of new materials, which must begin with an exploration of how sidechain configurations influence their phase behaviour. Here, dicatenar and hexacatenar derivatives of DPA and BPEA cores were synthesised in which the number and length of attached alkyl chains were varied in order to induce LC behaviour. The term 'catenar' refers to the number of alkyl chains attached to the central core. The resulting phase transition temperatures and LC behaviour were studied using differential scanning calorimetry (DSC) and polarised optical microscopy (POM), and spectroscopic properties were studied in solution and thin films. Amongst the non-LC derivatives whose melting and crystallisation temperatures we report as a function of side-chain length, we discovered a novel DPA derivative that exists as a non-volatile luminescent molecular liquid at room temperature. We also report a new LC derivative of BPEA that forms a nematic phase at 209°C.

2 Results and discussion

2.1 Synthesis

Five DPA derivatives were synthesised in three main steps according to Scheme 2, with full details and characterisation provided in the experimental section. Suzuki coupling of 4-methoxyphenylboronic acid and 9,10-dibromoanthracene was performed to obtain 9,10-dianisylanthracene **(1)** in good yield. The next step involved the deprotection of the outer methoxy groups. Hydrobromic acid was used for this, giving 9,10-bis(4-hydroxyphenyl)anthracene **(2)** as a hydroscopic green solid. The required alkyl chains were attached through Williamson ether synthesis to yield 9,10-bis(4-octyloxyphenyl)anthracene **(3)**, 9,10-bis(4-dodecyloxyphenyl)anthracene **(4)** and 9,10-bis(4-hexadecyloxyphenyl)anthracene **(5)**.

**Scheme 2** Synthesis of dicatenar 9,10-diphenylanthracene (DPA) derivatives
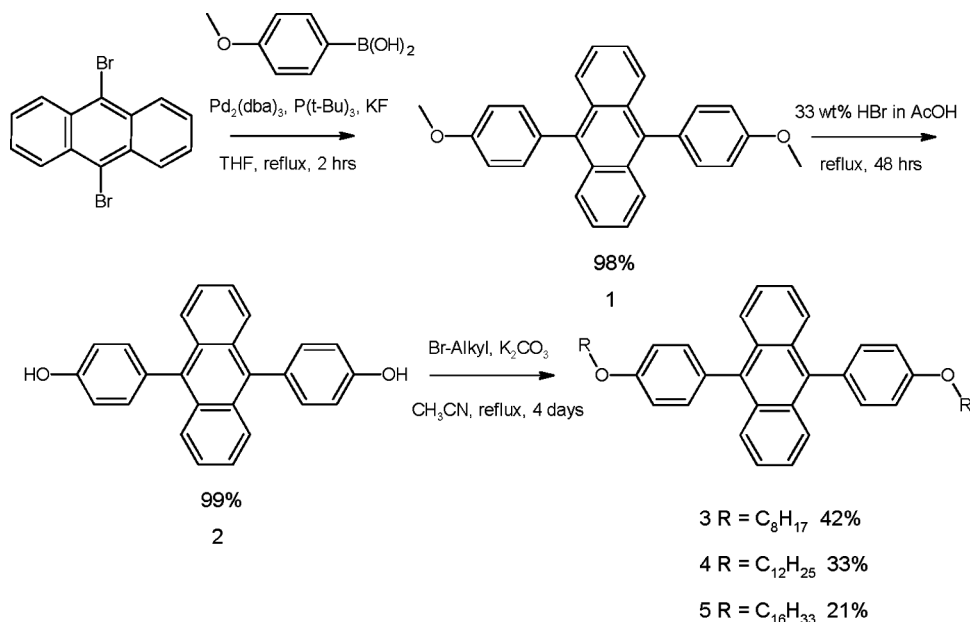
The syntheses of hexacatenar derivatives 9,10-bis{3,4,5-tris(decyloxy)phenyl}anthracene **(6)** and 9,10-bis{3,4,5-tris(hexadecyloxy)phenyl}anthracene **(7)** (Scheme 1) were performed using the same approach, except that the more reactive boron tribromide was required to cleave all three methoxy groups. The synthesis of these hexacatenar compounds is detailed in the experimental section.

Three derivatives of BPEA were synthesised via four main steps (Scheme 3). In contrast to the syntheses of DPA derivatives, tails were attached as the first step, owing to the more accommodating nature of the Sonogashira reaction. The molecule 4-hydroxyphenylbromide was treated with bromooctane at elevated temperatures to produce 4-octyloxyphenylbromide **(8)** as a colourless oil. All intermediates synthesised with this length chain were oils, and as a consequence all products were purified using column chromatography on silica. Compound **8** was reacted with trimethylsilylethynein

the presence of tetrakis(triphenylphosphine)palladium(0) and copper(I) iodide, which yielded 4-octyloxyphenyl(trimethylsilyl)ethyne, which was then deprotected with potassium hydroxide to yield 4-octyloxyphenylethyne **(9)**. Compound **9** was treated with 9,10-dibromoanthracene in the presence of tetrakis(triphenylphosphine)palladium(0) and copper iodide to yield 9,10-bis(4-octyloxyphenylethynyl)anthracene **(10)**, which was then purified by column chromatography on silica and recrystallised from CH$_3$Cl/MeOH. Purification was not completely effective, with a greasy residue remaining, identified by proton NMR peaks at 1.2–1.5 and 0.89 ppm.

Scheme 3 Synthesis of 9,10-bis(4-octyloxyphenylethynyl)anthracene
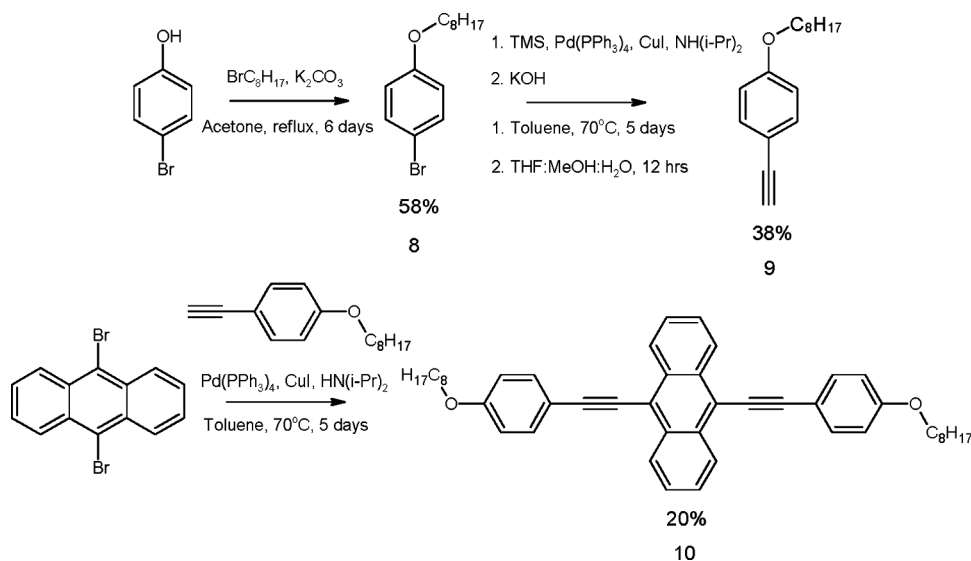
The synthesis in the same manner, but with hexadecyloxy chains resulted in the production of pure 9,10-bis(4-hexadecyloxyphenyl)anthracene **(11)**. 4-Ethynyl-4′-octyloxybiphenyl and 9,10-dibromoanthracene were synthesised via literature methods [10,12,13]. These two reactants were combined in a Sonogashira reaction to produce 9,10-bis(4′-octyloxybiphenyl-4-ylethynyl)anthracene **(12)**.

2.2   Phase behaviour

The phase behaviour of each of the compounds was investigated using DSC and POM. For the DPA dicatenar compounds **3**,**4** and **5**, the melting and crystallisation points decreased with increasing alkyl chain length, as shown in Table 1, however LC phases were not observed.

   The melting points of the hexacatenar DPA derivatives **6** and **7** were significantly lower, all transitions occurring under 50°C. Compound **7** did not form a LC phase, but compound **6** exhibited a novel supercooling property. The solid underwent melting, but would remain in the liquid state at room temperature for up to three days. The material underwent crystallisation at –23°C only upon reheating from –40°C. This is a novel non-volatile luminescent molecular liquid based on DPA, of which there are only two known examples at room temperature [14,15]. There are very few examples of stable

π-conjugated liquids [15–17]. This novel material could be exploited in photonic applications including upconversion, as it retains the flow of a liquid and enables diffusion through solution in a condensed state [12].

BPEA derivatives **10** and **11** did not form LC phases, exhibiting only melting and crystallisation, as shown in Table 2. Compound **10** decomposed around 150°C, which obscured the clear evaluation of melting around 135°C.

Compound **12** formed a nematic LC phase at 209.5°C, as shown in the POM image in Figure 1(a). When heated further, the compound did not form an isotropic phase but rather decomposed at 270°C. If not heated to decomposition, the material undergoes crystallisation into a mosaic-like crystalline solid on cooling, as shown in Figure 1(b).

Table 1 Phase transition temperatures and enthalpies of dicatenar DPA compounds

	Melting		Crystallisation	
Compound	*Temperature* (°C)	*Enthalpy* (Jg^{-1})	*Temperature* (°C)	*Enthalpy* (Jg^{-1})
3	169.65	–29.09	146.10	68.66
4	158.25	–75.48	141.07	88.56
5	147.88	–87.84	135.92	97.13
6	37.10	–	–23.00	–
7	39.46	–64.99	35.29	62.70

Table 2 Phase transition temperatures and enthalpies of BPEA compounds

	Melting		Crystallisation	
Compound	*Temperature* (°C)	*Enthalpy* (Jg^{-1})	*Temperature* (°C)	*Enthalpy* (Jg^{-1})
11	136.76	–135.02	132.68	138.75
12	209.54	–43.04	198.72	34.88

Figure 1 Polarised optical microscope images of compound **12** in a LC nematic phase at 240°C (a) and mosaic crystalline solid at 199°C (b) both using 40× magnification (see online version for colours)


(a)

(b)
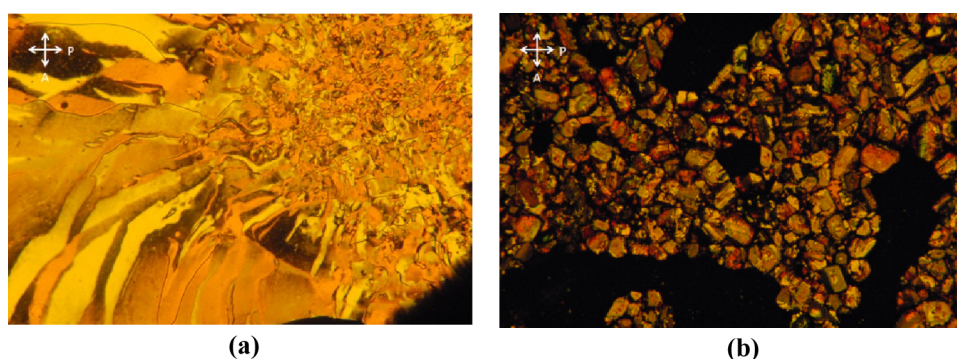
2.3 Spectroscopic properties

The solution phase absorption spectra of all DPA derivatives **3**–**7** did not vary significantly from that of the original DPA dye, retaining the pronounced vibronic

progression (hexacatenar derivatives shown in Figure 2(a)). The emission spectra exhibited only a slight red-shift compared with the parent DPA.

As found in the DSC measurements above, DPA derivative **6** could be melted and supercooled to remain as a neat liquid at room temperature. The absorption and emission spectra of this neat liquid are shown in Figure 2(b). Interestingly, the spectra did not vary significantly from the solution spectra, indicating that molecules condensed into the liquid state retain their monomeric character rather than aggregating. This property may be useful for photonic applications like photon upconversion. The high concentration and molecular diffusion found in a neat liquid promotes the excited state interactions that underpin upconversion, while the molecules retain favourable electronic excited state properties. Indeed, photon upconversion was recently demonstrated for one of the other known liquid DPA derivatives [14].

Figure 2   (a) Absorption and emission (dashed lines) spectra of the hexacatenar DPA derivatives in solution (7.5×10^{-5} M for absorption, 1×10^{-6} M for emission, with $\lambda_{ex} = 395$ nm). (b) Absorption and emission (dashed line) spectra of **6** as a neat liquid thin film (0.3 mg melted and spread on a glass substrate) (see online version for colours)

(a)

(b)
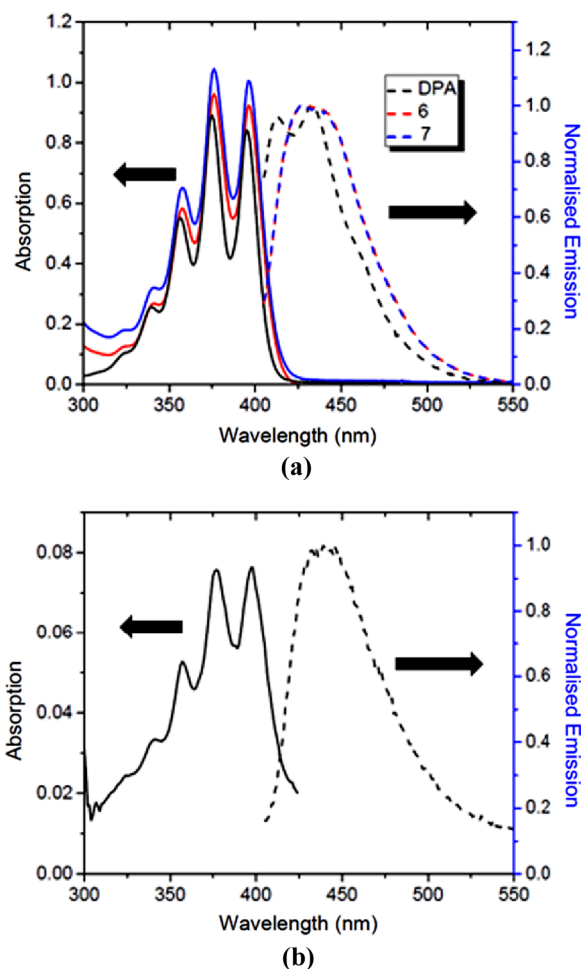
The absorption spectra of the dicatenar BPEA derivatives **10** and **11** did not vary significantly from the BPEA dye, which itself is red-shifted with respect to DPA owing to the extension of the π-system via the triple bond. However, the absorption and emission spectra of **12** (Figure 3(a)) were significantly shifted to longer wavelengths compared to the spectra of BPEA owing to the extension of the aromatic system via a phenyl ring.

Figure 3 (a) Absorption and emission spectra of compound **12** and BPEA in solution (5×10^{-5} M for absorption, 1×10^{-6} M for emission, with $\lambda_{ex} = 400$ nm). (b) Absorption and emission spectra ($\lambda_{ex} = 400$ nm) of a thin film of compound **12** after heating to 210°C, above the LC transition temperature, and recording spectra at subsequent time intervals (see online version for colours)

(a)

(b)
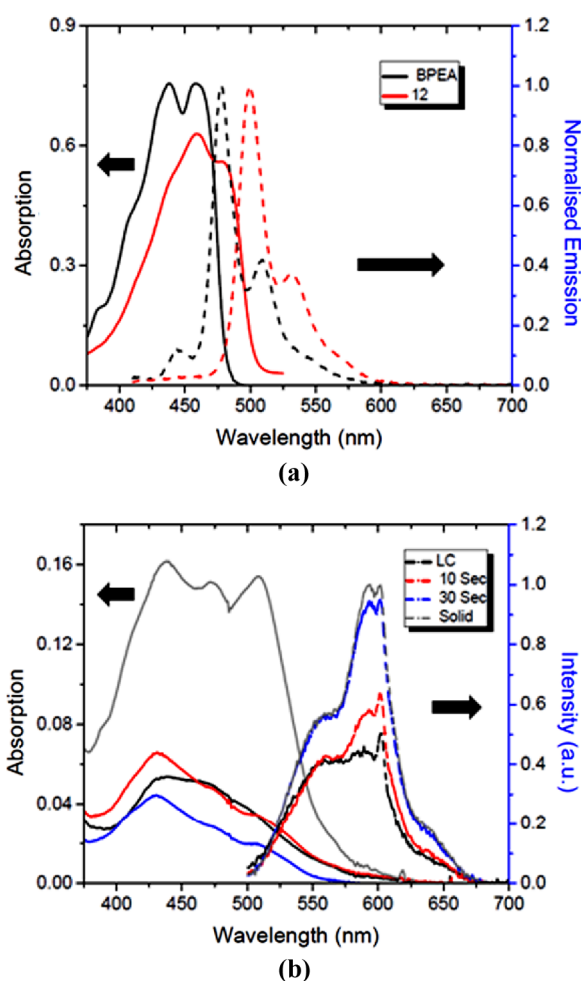
BPEA derivative **12**, the only LC derivative produced in this study, was dropcast from a solution of acetone to form a thin film on a glass substrate. The thin film was then heated to 210°C to study the spectroscopic properties of the LC phase. The absorption and emission spectra for the LC phase, shown in Figure 3(b), reveal a pronounced broadening, and washing out of the vibronic structure in solution (Figure 3(a)). Since the sample was removed from the hotplate during the course of spectroscopic measurements,

it rapidly crystallised, evidenced by the evolution of more structured peaks. Comparing the spectra for the LC phase to those of the solid crystalline phase revealed suppressed intensity at lower photon energy for the LC phase, for both absorption and emission spectra, suggesting suppression of excimer-like states that appear to characterise the solid crystal. The material was blended with palladium octaethylporphyrin, a common triplet sensitiser used to induce upconversion with anthracene derivatives [7,18]. The LC phase behaviour was retained with the dispersed sensitiser and the sensitiser did not decompose at such elevated temperatures. These observations bode well for the exploration of photon upconversion in LC anthracenes, however the high phase transition temperatures made it impractical to undertake more detailed photophysical studies. These results highlight the potential opportunities if LC anthracenes can be found with phase transition temperatures close to room temperature.

3   Conclusions

Eight new DPA and BPEA derivatives have been synthesised and their phase behaviours examined as a function of sidechain configurations in the search for LC properties. Symmetrical substitution of DPA derivatives did not result in LC phases, rather favouring the rigid ordering found in the crystalline solid, and exhibiting the predicted depression of melting point with increased alkyl chain length and number. A novel non-volatile luminescent molecular liquid was synthesised based on DPA. The material retained its monomeric spectroscopic properties in the condensed liquid state, which may be exploited in photonic applications such as upconversion. A LC BPEA derivative was synthesised, forming a mesophase at elevated temperatures. Its LC phase behaviour was retained upon dispersing a photon upconversion sensitiser, highlighting the promise of LC anthracenes for upconversion if materials with lower temperature LC phases can be discovered.

Acknowledgements

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Appendix

4　Experimental section

4.1　Synthesis of dicatenar DPA derivatives

*9,10-Dianisylanthracene **(1)***. Tris(dibenzylideneacetone)dipalladium(0) (0.06 g, 0.07 mmol), 4-methoxyphenylboronic acid (1.26 g, 8 mmol), 9,10-dibromoanthracene (1.13 g, 3.36 mmol), tri-*tert*-butylphosphonium tetrafluoroborate (0.04 g, 0.14 mmol), and potassium fluoride (1.45 g, 24 mmol) were transferred to a Schlenk tube under a nitrogen atmosphere. Dry tetrahydrofuran (12 mL) was added and the resulting mixture stirred

vigorously for 2 h. This reaction was quenched by addition of diethylether (40 mL). The product was obtained through purification by Soxhlet extraction (Yield: 1.22 g, 98%).

9,10-Bis(4-hydroxyphenyl)anthracene (2). Hydrobromic acid in acetic acid (33 w%, 20 mL, 121.5 mmol) was added dropwise to **1** (1.06 g, 2.7 mmol). The mixture was stirred and heated at reflux for 48 h. The resulting mixture was poured into an excess of distilled water and filtered through a silica frit. A hygroscopic green solid was obtained and dried *in vacuo* (Yield: 0.97 g, 99%).

9,10-Bis(4-octyloxyphenyl)anthracene (3). 1-Bromooctane (1.03 mL, 6 mmol) was added to a stirred solution of **2** (0.51 g, 1.4 mmol), potassium carbonate (0.69 g, 5 mmol) and acetonitrile (30 mL). The mixture was allowed to react at reflux for four days. The product was extracted with chloroform, and washed with water. The resulting organic layer was dried over anhydrous magnesium sulphate, filtered and dried *in vacuo*. The resulting product was recrystallised from methanol. (Yield: 0.35 g, 42%) ^{1}H NMR δ (500 MHz, CDCl$_3$): 7.75 (m, 4H, H1), 7.38 (d, $J = 8$ Hz, 4H, H6), 7.33 (m, 4H, H2), 7.13 (d, 4H, $J = 7$ Hz, H7), 4.11 (t, $J = 5$ Hz, 4H, H9), 1.89 (m, 4H, H10–H15), 1.55 (m, 4H, H10–H15), 1.5–1.2 (m, 16H, H10–H15), 0.92 (m, 6H, H16). Selected ^{13}C NMR δ (125 MHz, CDCl$_3$): 132.30 (s, C6), 125.19 (s, C2), 127.11 (s, C1), 114.36 (s, C7), 68.30 (s, C9), 26.11–31.87 (s, C10–C15), 14.18 (s, C16).
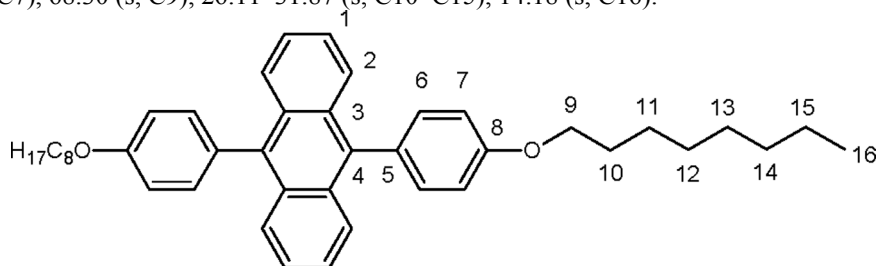
Compounds **4** and **5** were synthesised according to the method used for compound **3**.

4.2   Synthesis of DPA hexacatenar derivatives

3,4,5-Trimethoxyphenylboronic acid pinacol ester. 1.6 M n-butyllithium in hexane (15 mL, 0.024 mol) was added dropwise to a cooled flask (–78°C) of 1-bromo-3,4,5-trimethoxybenzene (5 g, 0.02 mol) in dry tetrahydrofuran (250 mL). The mixture was allowed to react for 1 h at –78°C. Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9.06 mL, 0.044 mol) was added, and the mixture warmed to room temperature and allowed to react overnight. The mixture was poured into a large amount of water and extracted with ethylacetate. The resulting organic layer was dried over anhydrous magnesium sulphate, filtered and the solvent removed *in vacuo*. (Yield: 4.46 g, 99%)

9,10-Bis(3,4,5-trimethoxyphenyl)anthracene.   Tris(dibenzylideneacetone)dipalladium(0) (0.22 g, 0.24 mmol), 3,4,5-trimethoxyphenylboronic acid pinacol ester (3.96 g, 13 mmol), 9,10-dibromoanthracene (2.82 g, 8.4 mmol), tri-*tert*-butylphosphonium tetrafluoroborate (0.28 g, 1 mmol), and potassium fluoride (2.92 g, 50 mmol) were transferred to a Schlenk tube. Dry tetrahydrofuran (65 mL) was added and the resulting mixture stirred vigorously at 50°C and the mixture left to react for 5 days. Solvent was removed *in vacuo* and the resulting crude powder extracted with water and chloroform. The organic layer was dried over anhydrous magnesium sulphate, filtered and solvent removed *in vacuo*. A yellow

powder was obtained which was further purified by column chromatography on silica using a solvent mix of 25% acetone in hexanes to yield the product. (Yield: 2.2 g, 51.3%) ^{1}H NMR δ (500 MHz, CDCl$_3$): 7.8 (m, 4H), 7.4 (m, 4H), 6.7 (s, 4H), 4.0 (s, 6H), 3.85 (s, 12H). ^{13}C NMR δ (125 MHz, CDCl$_3$): 153.5 (s,), 137.6 (s), 137.2 (2 singlets), 134.5 (s), 127 (s), 125.5 (s), 108.27 (s), 61.1 (s), 56.3 (s).

9,10-Bis{3,4,5-trihydroxyphenyl}anthracene. 9,10-bis(3,4,5-trimethoxyphenyl)anthracene (0.29 g, 0.57 mmol) was dissolved in dry dichloromethane in a Schlenk tube under nitrogen, and the resulting solution cooled to 0°C. A solution of boron tribromide in dichloromethane (5 mL, 1 M, 5 mmol) was added dropwise over 10 min, resulting in the formation of clear dark yellow-brown solution after 30 min. This solution was left to react for 2.5 h. Volatiles were removed *in vacuo*. The crude material was washed with water (2 × 3 mL) and thoroughly dried *in vacuo* with gentle heating. This material was used without further purification.

9,10-Bis{3,4,5-tris(decyloxy)phenyl}anthracene (6). 9,10-Bis(3,4,5-trihydroxyphenyl) anthracene was then suspended in dry dimethylformamide (10 mL) under nitrogen and potassium carbonate (0.6 g, 4.34 mmol), bromodecane (0.75 mL, 3.61 mmol) and dibenzo-18-crown-6 (0.002 g, 0.005 mmol) were added. The mixture was stirred and allowed to react at 70°C for 18 h. After cooling, the mixture was treated with water (20 mL), and the mixture extracted three times with dichloromethane (20 mL). The combined organic fractions were dried over anhydrous magnesium sulphate and solvent removed *in vacuo* leaving a brown oil that was further dried *in vacuo*. The crude material was purified by column chromatography on silica, eluting first with petroleum ether and progressively increasing the polarity of the eluent. A very pale yellow fraction eluted with almost pure acetone. This afforded 0.02 g pale yellow crystals of **6** on recrystallisation from chloroform/ethanol. Further crude product (0.057 g) was also recovered from the next column fraction but this was contaminated with a highly coloured impurity. (Yield: 0.02 g (pure material) + 0.057 g (crude), 10.7%) ^{1}H NMR δ (500 MHz, CDCl$_3$): 7.79 (m, 4H, H1), 7.36 (m, 4H, H2), 6.64 (s, 4H, H6), 4.13 (t, *J* = 5 Hz, 4H, H19), 3.94 (t, *J* = 10 Hz, 8H, H8), 1.89 (q, 4H, H20), 1.79 (q, 8H, H9), 1.57–1.2 (m, 84H, H10–H16 and H20–H27), 0.87 (m, 18H, H17 and H28).
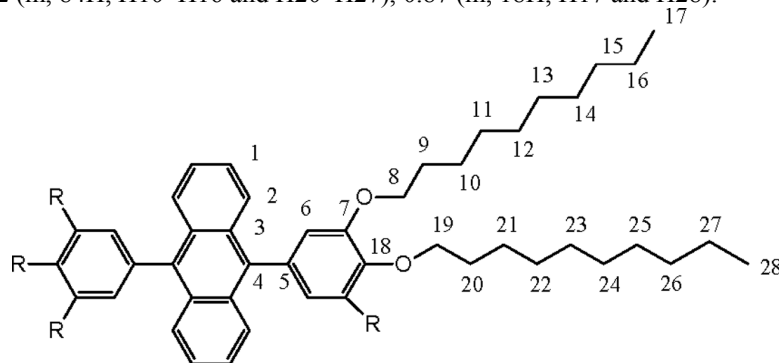
Where R = OC$_{10}$H$_{22}$

The synthesis of compound **7** was completed using the same methods as for compound **6**.

4.3   Synthesis of BPEA derivatives

4-Octyloxyphenyl bromide (8). 4-Hydroxyphenyl bromide (2 g, 11.5 mmol), potassium carbonate (2.8 g, 20.5 mmol), bromooctane (2.97 mL, 17.25 mmol) and acetone (100 mL) were combined and allowed to react at 50°C for six days. The reaction mixture was poured into an excess of water and extracted with hexanes. This was further purified through column chromatography on silica using a solvent mix of 10% dichloromethane in hexanes to yield a colourless oil. (Yield: 1.91 g, 58.2%)

4-Octyloxyphenyl(trimethylsilyl)ethyne. 4-Octyloxyphenyl bromide (1.9 g, 6.69 mmol), copper iodide (0.064 g, 0.33 mmol), tetrakis(triphenylphosphine)palladium(0) (0.39 g, 0.33 mmol), di-isopropylamine (1.2 mL, 8.5 mmol) and trimethylsilylethyne (1.2 mL, 8.5 mmol) were combined in dry toluene (20 mL) and allowed to react for five days at 70°C. The reaction mixture was diluted with dichloromethane, washed with an aqueous solution of ammonium chloride (saturated). The resulting organic layer was dried over anhydrous magnesium sulphate, filtered and solvent removed *in vacuo* to yield a pale yellow oil. This was purified through column chromatography on silica using a solvent mix of 10% dichloromethane in hexanes. (Yield: 0.92 g, 61.6%)

4-Octyloxyphenylethyne (9). 4-Octyloxyphenyl(trimethylsilyl)ethyne(0.49 g, 1.63 mmol) and potassium hydroxide (0.86 g, 15.4 mmol) were combined in a solvent mixture of tetrahydrofuran : methanol : water (4 mL : 4 mL : 1 mL) and stirred overnight at room temperature. The reaction mixture was diluted with water and extracted with dichloromethane. The organic layer was dried over anhydrous magnesium sulphate, filtered and dried *in vacuo* to yield an orange oil. This was purified through column chromatography on silica using a solvent mix of 1% ethyl acetate in hexanes. (Yield: 0.29 g, 37.5%)

9,10-Bis{4-(octyloxy)phenylethynyl}anthracene(10). 4-Octyloxyphenylethyne (0.47 g, 2.02 mmol), 9,10-dibromoanthracene (0.31 g, 0.92 mmol), copper iodide (0.02 g, 0.1 mmol), tetrakis(triphenylphosphine)palladium(0) (0.12 g, 0.1 mmmol), di-isopropylamine (0.46 mL, 3.28 mmol) were combined in dry toluene (20 mL) and allowed to react for five days at 70°C. Solvent was removed *in vacuo*, and crude purified by column chromatography on silica with using hexanes as the eluent. This material was recrystallised from CHCl$_3$/MeOH. (Yield: 0.26 g, 20.1%) ^{1}H NMR δ (500 MHz, CDCl$_3$): 8.69 (m, 4H, H1), 7.7 (d, *J* = 9 Hz, 4H, H3), 7.62 (m, 4H, H2), 6.97 (d, *J* = 8.4 Hz, 4H, H4), 4.03 (t, *J* = 6.6 Hz, 4H, H5), 1.81 (m, 4H, H6), 1.5–1.2 (m, 20H, H7–H11), 0.87 (m, 6H, H12).
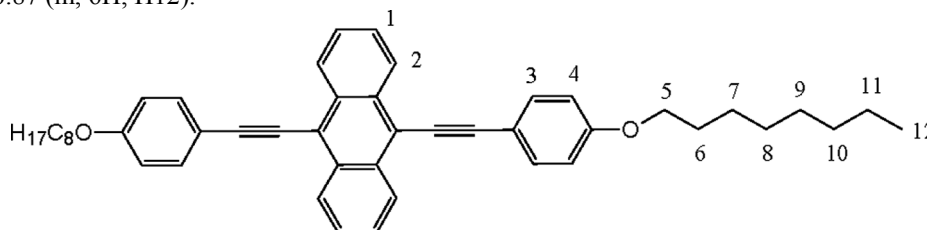
9,10-Bis(4'-octyloxybiphenyl-4-ylethynyl)anthracene (12). 4-Ethynyl-4′-octyloxybiphenyl (0.51 g, 1.6 mmol), 9,10-dibromoanthracene (0.27 g, 0.8 mmol), tetrakis (triphenylphosphine)palladium(0) (55 mg, 0.048 mmol), copper(I) iodide (6 mg,

0.032 mmol), diisopropylamine (0.67 mL, 4.8 mmol) and tetrahydrofuran (8 mL) were combined in a flask equipped with a large magnetic stir-bar and condenser under an argon atmosphere and heated to 60°C for 24 h. The solvent was removed from the resulting mixture of orange solid and fluorescent yellow solution under reduced pressure. The solid was suspended in dichloromethane (40 mL), washed with water (2 × 40 mL), and the solvent removed under reduced pressure. The resulting orange solid was recrystallised from a minimum of boiling chloroform, giving pure compound **12** (0.36 g, 57%). ^{1}H NMR δ (500 MHz, CDCl$_3$): 8.73 (m, 4H, anth), 7.83 (dm, J = 8.3 Hz, 4H, Ph), 7.66 (m, 8H, anth& Ph), 7.60 (dm, J = 8.5 Hz, 4H, Ph), 7.01 (dm, J = 8.8 Hz, 4H, Ph), 4.03 (t, J = 6.5 Hz, 4H, OCH$_2$), 1.83 (quin, J = 7.6 Hz, 4H, CH$_2$), 1.49 (quin, J = 7.8 Hz, 4H, CH$_2$), 1.34 (m, 16H, (CH$_2$)$_4$), 0.90 (t, J = 7.0 Hz, 6H, CH$_3$).

Phase Behaviour. A Shimadzu DSC-60 calibrated with metallic indium supplied by Mettler-Toledo was used. Samples of between 5-10 mg were analysed in crimped aluminium pans, and measured against an empty aluminium reference pan under nitrogen atmosphere, and the data processed using Shimadzu TA-60 thermal data analysis software. In the case of the decylhexacatenar DPA derivative, that measurement was performed on a Thermal Associates DSC-Q100, which could cool down to –80°C. All samples with a heating rate of 1°C min^{-1} unless otherwise stated.

A Nikon Optishot-2 polarising microscope, fitted with a Nikon D200 DSLR 10.3 megapixel camera was used. Samples were prepared by placing a small amount of sample (mg) on a slide and covering with a cover slip. The temperature of the sample was adjusted by using a Mettler-Toledo FP82HT hot stage.

Spectroscopy. Solution samples were diluted to the appropriate concentration in spectroscopic grade toluene. Absorption spectra were obtained using an Agilent diode array, baseline corrected, UV–Vis spectrophotometer, with two-sided quartz cuvettes unless otherwise stated. Emission spectra were obtained on a Shimadzu RF-5301PC Spectrofluorophotometer, with four-clear sided quartz cuvettes unless otherwise stated.