Supporting information for

**Mesogenic BODIPYs: The investigation of the correlation between liquid crystalline behaviour and fluorescence intensity**

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S1: Experimental

Transition temperatures and enthalpies were determined using a Mettler DSC822e differential scanning calorimeter with STARe software, under nitrogen/helium, at a rate of 10°C/min, calibrated with indium (156.6°C, 28.45J g⁻¹) and using an aluminium reference. Optical studies were carried out using an Olympus BH-2 optical polarising microscope equipped with a Mettler FP82 HT hot stage and a Mettler FP90 central processor. Photograph images of the mesophases were taken using a JVC digital video camera connected to a PC. Software Studio Capture, supplied by Studio86Designs, was used for image capturing.

NMR spectra were recorded on a Jeol JNM ECP400 spectrometer, with TMS δ_H = 0 as the internal standard or residual protic solvent. [CDCl₃, δ_H = 7.26; CD₃OD, δ_H = 3.30]. Chemical shifts are given in ppm (δ) and coupling constants (J) are given in Hertz (Hz). ¹H-NMR were recorded at 400 MHz; ¹³C-NMR recorded at 100.5 MHz; ¹¹B-NMR recorded at 128.3 MHz.

UV-visible spectra were measured on a Varian Cary 50 Bio UV-visible Spectrophotometer and an ATI Unicam UV2-100 spectrometer. Fluorescence spectra were measured using a Jobin-Yvon Horiba Fluorolog 3-22 Tau-3 spectrofluorometer with a right angle illumination method. All measurements were carried out in a 4-sided quartz cuvette of 10mm diameter. Lifetime measurements were obtained via the time-correlated single photon counting technique. Samples were excited by a Nd:YAG laser (at an excitation wavelength of 532 nm). Emission was collected at 90° to the source of excitation. The emission wavelength was selected by a monochromator (Jobin Yvon Triax 190). All measurements were performed in a four-sided cuvette using an absorbance value of 0.1, which was measured and checked using the Unicam spectrometer. The Fluorescence lifetime values were quoted to 1 decimal place. Fluorescence quantum yields with an absorbance at the maximum typically below 0.2 were determined by use of an integrating sphere with a HORIBA Jobin-Yvon Fluorolog FL3-22 Tau-3, following a method described in the literature. All measurements, unless
stated, were obtained at 298 K and aerated. The dye-doped liquid crystal measurements were acquired by excitation of BODIPY-doped BL024 incorporated into a twisted nematic cell with a Ti:Saph laser (at an excitation wavelength of 300 nm in order to avoid spectral overlap of the excitation beam and the BODIPY emission). Emission of these samples was collected parallel to the source of excitation.

Thin-layer chromatography (TLC) was performed using Merck aluminium plates coated with silica gel 60 F254 and visualised under UV light or using potassium permanganate solution. Column chromatography was performed using MP Silica 32-63, 60 Å. All solvent mixtures are given in v/v ratios.

4-Hydroxybenzoic acid, 11-bromoundecanol, DMAP and 4-iodobenzoic acid were purchased from Alfa Aesar and used as received. Sodium hydroxide, DCC, copper (I) iodide, triethylamine and (2-biphenyl)di-tert-butylphosphine were purchased from Sigma Aldrich and used as received. 4’-(11-Hydroxyundecyl)-biphenyl-4-carbonitrile was purchased from TCI Europe and used as received. 4-Carboxyphenylboronic acid pinacol ester was purchased from Frontier Scientific and used as received. All solvents and desiccants were purchased from Fisher Scientific and used as received. Dibenzylideneacetone palladium (II) and bis(triphenylphosphine)palladium (II) chloride were purchased from Strem Chemicals and used as received.

The microwave-assisted reactions were carried out in a CEM Discover System.

**8-(4-Bromophenyl)-BODIPY (A):**

4-Bromobenzaldehyde (5g, 0.027mol) was dissolved in pyrrole (75ml) and the solution was degassed with nitrogen for 20mins. TFA (0.2ml) was then added and the mixture was stirred for 20mins. The pyrrole was removed *in vacuo* and dichloromethane (100ml) was then added and the solution was washed with sat. Na2CO3(aq) (50ml) and water (2 x 50ml), dried over MgSO4 and evaporated. The residue was redissolved in dichloromethane (100ml) and chloranil (6.64g) was added and the mixture was stirred for 16hrs.
Diisopropylethylamine (25.87ml) was then added followed by boron trifluoride diethyl etherate (24.99ml) and the mixture was stirred under nitrogen for 16hrs. The solution was then washed with 2% HCl(aq) (75ml) and water (3 x 75ml), dried over anhydrous MgSO₄ and evaporated in vacuo. The residue was purified by column chromatography eluting with 4:6 hexane:CH₂Cl₂ to yield the product as a red solid (0.52g, 6%), m.p. 202-203°C, lit. 202-203°C²⁹.

¹H-NMR [400MHz, CDCl₃] δ 6.56 (2H, m, Py-H), 6.91 (2H, m, Py-H), 7.45 (2H, d, Ph-H, J = 8.61Hz), 7.67 (2H, d, Ph-H, J = 8.61Hz), 7.96 (2H, m, Py-H).

¹³C-NMR [100MHz, CDCl₃] δ 118.8, 125.5, 131.3, 131.8, 132.7, 134.7, 144.6, 145.8.

¹¹B-NMR [128.3MHz, CDCl₃] δ -0.49.

HRMS (ESI) = calc. 368.9981 and 370.9960, found. 368.9984 and 370.9963 (M + Na⁺).

8-(4-Iodophenyl)-1,3,5,7-tetramethyl-BODIPY (B):

4-Iodobenzoyl chloride (2g, 7.51mmol) and 2,4-dimethylpyrrole (1.55ml, 15.2mmol) were dissolved in dry dichloromethane (60ml) and the solution was refluxed under nitrogen for 3hrs. The solution was cooled to r.t. and triethylamine (4.88ml, 35mmol) was then added followed by boron trifluoride diethyl etherate (5.01ml, 39.5mmol) and the solution was stirred at r.t. for 16hrs. The solution was then washed with water (3 x 50ml) and dried over anhydrous MgSO₄ and evaporated in vacuo. The residue was purified by column chromatography eluting with 1:1 hexane:CHCl₃ to yield the pure product as a bright orange solid (1.18g, 35%), m.p. 213-214°C, lit. 213-215°C³⁰.

¹H-NMR [400MHz, CDCl₃] δ 1.42 (6H, s, 2 x CH₃), 2.55 (6H, s, 2 x CH₃), 5.99 (2H, s, Py-H), 7.04 (2H, d, Ph-H, J = 8.43Hz), 7.85 (2H, d, Ph-H, J = 8.43Hz).
$^{13}$C-NMR [100MHz, CDCl$_3$] δ 14.59, 14.65, 94.7, 121.4, 129.9, 131.1, 134.6, 138.3, 142.9, 155.9.

$^{11}$B-NMR [128.3MHz, CDCl$_3$] δ -0.2446.


**8-(4-Iodophenyl)-1,3,5,7-tetramethyl-2,6-diethyl-BODIPY (C):**

4-Iodobenzoyl chloride (2g, 7.51mmol) and kryptopyrrole (2.03ml, 15.02mmol) were dissolved in dry dichloromethane (60ml) and the solution was heated at reflux under nitrogen for 3hrs. The solution was cooled to r.t. and triethylamine (4.88ml, 35.0mmol) was then added followed by boron trifluoride diethyl etherate (5.01ml, 39.5mmol) and the solution was stirred under nitrogen for 18hrs. The solution was then washed with water (4 x 50ml), dried over anhydrous MgSO$_4$ and evaporated *in vacuo*. The residue was passed through a short silica column eluting with 1:4 hexane:toluene and evaporated *in vacuo*. The crude product was purified by column chromatography eluting with 1:4 CH$_2$Cl$_2$:hexane after dry loading to yield the pure product as a bright red solid (1.36g, 36%), m.p. 290°C (decomp.).

$^1$H-NMR [400MHz, CDCl$_3$] δ 0.98 (6H, t, 2 x CH$_3$CH$_2$, $J = 7.52$Hz), 1.31 (6H, s, 2 x CH$_3$), 2.29 (4H, q, 2 x CH$_2$CH$_3$, $J = 7.57$Hz), 2.52 (6H, s, 2 x CH$_3$), 7.04 (2H, d, Ph-H, $J = 7.88$Hz), 7.83 (2H, d, Ph-H, $J = 7.88$Hz).

$^{13}$C-NMR [100MHz, CDCl$_3$] δ 11.9, 12.5, 14.6, 17.1, 94.4, 130.3, 133.0, 135.4, 138.2, 154.1.

$^{11}$B-NMR [128.3MHz, CDCl$_3$] δ 0.0000.

HRMS (ESI) = calc. 507.1279, found 507.1269 (M + H$^+$).
**8-(4-Trimethylsilylethynylphenyl)-BODIPY:**

4-[(Trimethylsilyl)ethynyl]benzaldehyde (2g, 9.89mmol) was dissolved in freshly distilled pyrrole (17.2ml, 0.25mol) and the mixture was degassed with argon for 15mins. TFA (0.1ml) was then added and the mixture was stirred at r.t. under argon for 15mins. The excess pyrrole was then distilled off under reduced pressure. The oily residue was then passed through a short silica plug eluting with dichloromethane to remove the pyrrolic by-products. The solvent was removed and redissolved in dry dichloromethane (50ml) and chloranil (2.43g, 9.89mmol) was then added and the mixture was stirred at r.t. for 15hrs. Diisopropylethylamine (18.95ml, 0.11mol) was then added followed by boron trifluoride diethyl etherate (18.79ml, 0.15mol). The solution was then stirred at r.t. for 16hrs. The solution was then filtered through a pad of celite and the filtrate was washed with water (4 x 75ml), dried over anhydrous MgSO4, filtered and evaporated *in vacuo*. The residue was purified by column chromatography eluting with 5:95 EtOAc:CH2Cl2 to yield the product as dark red needles (494mg, 14%), m.p. 140-141°C.

$^1$H-NMR [400MHz, CDCl3] δ 0.22 (9H, s, Si(CH3)3), 6.48 (2H, m, Py-H), 6.83 (2H, m, Py-H), 7.45 (2H, d, Ph-H, $J = 8.43$Hz), 7.55 (2H, d, Ph-H, $J = 8.43$Hz), 7.88 (2H, m, Py-H).

$^{13}$C-NMR [100MHz, CDCl3] δ 97.8, 103.9, 118.8, 126.1, 130.5, 131.5, 132.1, 132.8, 144.5.

$^{11}$B-NMR [128.3MHz, CDCl3] δ -0.49.

HRMS (ESI) = calc. 365.1452, found. 365.1458 (M + H+).

**8-(4-Ethynylphenyl)-BODIPY (D):**

8-(4-Trimethylsilylethynylphenyl)-BODIPY (390mg, 1.07mmol) was dissolved in THF (30ml) and TBAF (0.48g, 2.14mmol) was then added and the solution was stirred at r.t.
for 15hrs. The THF was then removed in vacuo and the residue dissolved in dichloromethane (50ml) and washed with 2% HCl(aq) (30ml) and water (2 x 30ml) followed by drying over anhydrous MgSO₄, filtration and evaporation in vacuo. The residue was purified by column chromatography eluting with 1:1 CH₂Cl₂:hexane to yield the product as a bright red solid (185mg, 59%), m.p. 182-183°C.

1H-NMR [400MHz, CDCl₃] δ 3.19 (1H, s, H-C≡C), 6.49 (2H, m, Py-H), 6.84 (2H, m, Py-H), 7.47 (2H, d, Ph-H, J = 8.44Hz), 7.58 (2H, d, Ph-H, J = 8.44Hz), 7.89 (2H, m, Py-H).

13C-NMR [100MHz, CDCl₃] δ 77.0, 79.7, 115.9, 122.0, 127.5, 128.5, 129.3, 131.2, 131.8, 141.6.

11B-NMR [128.3MHz, CDCl₃] δ -0.73

MS (ESI) = 292.0 (M⁺).

**8-(4-Trimethylsilylethynylphenyl)-1,3,5,7-tetramethyl-BODIPY:**

4-[Trimethylsilyl]ethynylbenzaldehyde (1.4g, 6.92mmol) and 2,4-dimethylpyrrole (1.43ml, 13.8mmol) were dissolved in dry dichloromethane (70ml) and degassed with argon for 20mins. TFA (0.1ml) was then added and the solution was stirred at r.t. under nitrogen for 16hrs. DDQ (1.57g, 6.92mmol) was then added and the solution was stirred at r.t. for 5hrs. Triethylamine (4.82ml, 34.6mmol) and boron trifluoride diethyl etherate (5.70ml, 45.0mmol) were then added and the solution was stirred at r.t. for 16hrs. The solution was then washed with water (4 x 50ml), dried over anhydrous MgSO₄ and evaporated in vacuo. The residue was then passed through a short silica column eluting with 1:1 hexane:CH₂Cl₂ and evaporated in vacuo. The residue was then purified by column chromatography eluting with 3:2 hexane:CH₂Cl₂ to yield the pure product as a bright red solid (299mg, 10%), m.p. 214-215°C.
$^1$H-NMR [400MHz, CDCl$_3$] δ 0.21 (9H, s, Me$_3$Si), 1.32 (6H, s, 2 x CH$_3$), 2.48 (6H, s, 2 x CH$_3$), 5.91 (2H, s, Py-H), 7.17 (2H, d, Ph-H, $J = 8.44$Hz), 7.53 (2H, d, Ph-H, $J = 8.44$Hz).

$^{13}$C-NMR [100MHz, CDCl$_3$] δ 14.7, 95.9, 104.3, 121.5, 124.0, 128.2, 132.8, 135.3, 143.1, 155.9.

$^{11}$B-NMR [128.3MHz, CDCl$_3$] δ -0.3060.

HRMS (ESI) = calc. 365.1452, found. 365.1458 (M + H$^+$).

**8-(4-Ethynylphenyl)-1,3,5,7-tetramethyl-BODIPY (E):**

5-(4-Trimethylsilylethynylphenyl)-2,4,6,8-tetramethyl-BODIPY (250mg, 0.595mmol) was dissolved in methanol (20ml) and anhydrous potassium carbonate (8mg, 59.5μmol) was added and the mixture was stirred at r.t. for 16hrs. Dichloromethane (80ml) was then added and the mixture was washed with water (3 x 50ml), dried over anhydrous MgSO$_4$ and evaporated in vacuo. The residue was purified by column chromatography eluting with 3:2 hexane:CH$_2$Cl$_2$ to yield the pure product as a bright red solid (137mg, 66%), m.p. 252-253°C, lit. 251-252°C, lit. 252-254°C$^{31}$.

$^1$H-NMR [400MHz, CDCl$_3$] δ 1.40 (6H, s, 2 x CH$_3$), 2.55 (6H, s, 2 x CH$_3$), 3.18 (1H, s, C≡CH), 5.99 (2H, s, Py-H), 7.27 (2H, d, Ph-H, $J = 8.13$Hz), 7.63 (2H, d, Ph-H, $J = 8.44$Hz).

$^{13}$C-NMR [100MHz, CDCl$_3$] δ 13.0, 77.0, 81.3, 119.8, 121.4, 126.7, 131.3, 134.0, 135.6, 141.4, 154.3.

$^{11}$B-NMR [128.3MHz, CDCl$_3$] δ -0.2205.

HRMS (ESI) = calc. 349.1682, found 349.1688 (M$^+$).
8-(4-Ethynylphenyl)-1,3,5,7-tetramethyl-2,6-diethyl-BODIPY (F):

4-[(Trimethylsilyl)ethynyl]benzaldehyde (2g, 9.89mmol) and kryptopyrrole (2.74ml, 20.3mmol) were dissolved in dry dichloromethane (100ml) and degassed with argon for 15mins. TFA (0.1ml) was then added and the solution was stirred at r.t. under argon for 16hrs. Chloranil (2.43g, 9.89mmol) was then added and the mixture stirred at r.t. for 4hrs. Triethylamine (6.89ml, 49.6mmol) was then added, followed by boron trifluoride diethyl etherate (3.66ml, 29.7mmol) and the solution stirred at r.t. under argon for 17hrs. The solution was then washed with water (4 x 80ml), dried over anhydrous MgSO₄, filtered and evaporated in vacuo. The residue was passed through a short silica column eluting with 2:3 CH₂Cl₂:hexane to remove the pyrrolic by-products. The collected fractions were then dissolved in methanol (15ml) and anhydrous potassium carbonate (15mg, cat.) was added to the solution which was then stirred at r.t. for 16hrs. The methanol was evaporated in vacuo and the residue was purified by column chromatography eluting with 1:1 CH₂Cl₂:hexane to yield the pure product as a red solid (309mg, 10%), m.p. 249-250°C, lit. 250°C³².

¹H-NMR [400MHz, CDCl₃] δ 0.97 (6H, t, CH₃CH₂, J = 7.61Hz), 1.29 (6H, s, 2 x Me), 2.29 (4H, q, CH₃CH₂, J = 7.51Hz), 2.52 (6H, s, 2 x Me), 3.18 (1H, s, HCC-Ph), 7.26 (2H, d, Ph-H, J = 8.43Hz), 7.61 (2H, d, Ph-H, J = 8.43Hz).

¹³C-NMR [100MHz, CDCl₃] δ 10.5, 11.1, 13.2, 15.7, 19.4, 119.3, 121.3, 127.1, 131.4, 131.6, 135.1, 136.8, 152.7.

¹¹B-NMR [128.3MHz, CDCl₃] δ -0.1224.

HRMS (ESI) = calc. 405.2308, found. 405.2311 (M + H⁺).
4-(11-Hydroxyundecyloxy)-benzoic acid:

4-Hydroxybenzoic acid (6g, 0.043mol) and sodium hydroxide (3.44g in 21ml water) was dissolved in ethanol (100ml) and heated to reflux. 11-Bromoundecanol (8.25g, 0.033mol) in ethanol (25ml) was then added dropwise. Once addition was complete, the mixture was refluxed for 16hrs. The mixture was then cooled to r.t. and the ethanol was removed in vacuo. Water (150ml) was then added and the solution acidified with conc. HCl (aq) and the resulting precipitate filtered off and recrystallized from isopropanol to yield the pure product as a white solid (7.28g, 72%) m.p. 108-110°C (lit. 110°C33).

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\begin{align*}
\text{1H-NMR [CD}_3\text{OD, }400\text{MHz}] & \quad \delta 1.32 (12\text{H, m, CH}_2\text{'s}), 1.50 (4\text{H, m, CH}_2\text{'s}) 1.78 (2\text{H, m, CH}_2), 3.53 (2\text{H, t, CH}_2\text{OH, }J = 6.57\text{Hz}), 4.03 (2\text{H, t, CH}_2\text{O, }J = 6.57\text{Hz}), 6.96 (2\text{H, d, Ph-H, }J = 9.07\text{Hz}), 7.95 (2\text{H, d, Ph-H, }J = 9.07\text{Hz}).
\end{align*}
\]

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\begin{align*}
\text{13C-NMR [CD}_3\text{OD, }100\text{MHz}] & \quad \delta 26.9, 30.59, 30.64, 30.68, 33.7, 63.0, 69.3, 115.1, 123.8, 132.8, 164.6, 169.9.
\end{align*}
\]

HRMS (ESI) = calc. 309.2060, found 309.2063 (M + H+).

4-(11-Hydroxyundecyloxy)-phenyl-4′-cyano-4-biphenyl carboxylate:

4-(11-Hydroxyundecyloxy)benzoic acid (2g, 6.48mmol) and 4′-(11-hydroxyundecyl)-biphenyl-4-carbonitrile (1.29g, 6.61mmol) were dissolved in dry dichloromethane (80ml). DCC (2.27g, 0.088mol) and DMAP (0.82g, 6.68mmol) were then added and the mixture was stirred under nitrogen for 20hrs. The mixture was then filtered and the filtrate washed with 2% HCl (aq) (50ml), sat. Na₂CO₃(aq) (50ml) and water (2 x 50ml), dried over MgSO₄, filtered and evaporated. The residue was recrystallized from ethyl acetate to yield the pure product as a white solid (2.11g, 67%), Cr 125 N 175 I.

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\begin{align*}
\text{1H-NMR [CDCl}_3, 400\text{MHz}] & \quad \delta 1.29 (12\text{H, m, CH}_2), 1.46 (4\text{H, m, CH}_2), 1.81 (2\text{H, m, CH}_2), 3.63 (2\text{H, t, CH}_2\text{OH, }J = 6.72\text{Hz}), 4.03 (2\text{H, t, CH}_2\text{OPh, }J = 6.72\text{Hz}), 6.96 (2\text{H, d, Ph-H, }J
\end{align*}
\]

HRMS (ESI) = calc. 309.2060, found 309.2063 (M + H+).
4-(11-Carboxy-(4-[boronic acid pinacolate]-phenyl))-phenyl-4'-cyano-4-biphenyl carboxylate (G):

4-(11-Hydroxyundecyloxy)-phenyl-4'-cyano-4-biphenyl carboxylate (0.80g, 1.64mmol), 4-carboxyphenylboronic acid pinacol ester (0.40g, 1.61mmol), DCC (0.56g, 2.74mmol) and DMAP (0.20g, 1.66mmol) were dissolved in dry dichloromethane (50ml) and the solution was stirred at r.t. for 16hrs. The precipitate was then filtered off and the filtrate was washed with 2% HCl (aq) (40ml) and water (2 x 40ml), dried over MgSO 4 and evaporated. The residue was then recrystallized from ethyl acetate to yield the pure product as a white crystalline solid (0.80g, 78%).

1H-NMR [400MHz, CDCl3] δ 1.33 (10H, m, CH2’s), 1.36 (12H, s, 4 x CH3), 1.47 (4H, m, CH2’s), 1.80 (4H, m, CH2’s), 4.06 (2H, t, CH2OPh, J = 6.51Hz), 4.33 (2H, t, CH2O, J = 6.78Hz), 6.99 (2H, d, Ph-H, J = 8.98Hz), 7.34 (2H, d, Ph-H, J = 8.61Hz), 7.65 (2H, d, Ph-H, J = 8.80Hz), 7.70 (2H, d, Ph-H, J = 8.61Hz), 7.75 (2H, d, Ph-H, J = 8.61Hz), 7.87 (2H, d, Ph-H, J = 8.43Hz), 8.03 (2H, d, Ph-H, J = 8.43Hz), 8.16 (2H, d, Ph-H, J = 8.98Hz).

13C-NMR [100MHz, CDCl3] δ 24.9, 26.0, 28.7, 29.1, 29.2, 29.3, 29.5, 65.2, 68.4, 84.2, 111.0, 114.4, 118.9, 121.2, 122.6, 127.7, 128.3, 128.5, 132.3, 132.6, 132.7, 134.6, 136.7, 144.9, 151.6, 163.7, 164.8, 166.7.

11B-NMR [128.3MHz, CDCl3] δ 29.74.
HRMS (ESI) = calc. 733.4026, found 733.4011 (M + NH$_4^+$).

4-(11-Carboxy-(4-iodophenyl))-phenyl-4’-cyano-4-biphenyl carboxylate (H):

4-Iodobenzoic acid (0.32g, 1.29mmol) and 4-(11-hydroxyundecyloxy)-phenyl-4’-cyano-4-biphenyl carboxylate (11) (0.63g, 1.31mmol) were dissolved in dry dichloromethane (75ml). DCC (0.45g, 2.19mmol) and DMAP (0.16g, 1.33mmol) were then added and the solution was stirred under nitrogen for 16hrs. The mixture was then filtered and the filtrate was washed with 2% HCl$_{(aq)}$ (50ml) and water (2 x 50ml), dried over MgSO$_4$ and evaporated. The residue was the recrystallized from ethyl acetate to yield the pure product as a white solid (0.65g, 71%).

$^1$H-NMR [400MHz, CDCl$_3$] $\delta$ 1.30 (10H, m, CH$_2$’s), 1.73 (8H, m, CH$_2$’s), 4.04 (2H, t, CH$_2$OPh, $J$ = 6.57Hz), 4.29 (2H, t, CH$_2$O, $J$ = 6.72Hz), 6.97 (2H, d, Ph-H, $J$ = 9.07Hz), 7.31 (2H, d, Ph-H, $J$ = 8.76Hz), 7.62 (2H, d, Ph-H, $J$ = 8.76Hz), 7.67 (2H, d, Ph-H, $J$ = 8.44Hz), 7.73 (4H, d, Ph-H, $J$ = 8.76Hz), 7.77 (2H, d, Ph-H, $J$ = 8.76Hz), 8.14 (2H, d, Ph-H, $J$ = 8.76Hz).

$^{13}$C-NMR [100MHz, CDCl$_3$] $\delta$ 26.0, 29.01, 29.08, 29.2, 29.5, 65.4, 68.4, 111.0, 114.4, 118.9, 121.2, 122.6, 127.7, 128.3, 131.0, 132.3, 132.6, 137.7, 144.9, 151.6, 163.7, 164.9.

HRMS (ESI) = calc. 733.2133, found 733.2132 (M + NH$_4^+$).

**Compound 1:**

A (50mg, 0.144mmol), G (109mg, 0.173mmol), dibenzylideneacetone palladium (II) (36mg, 39.6$\mu$mol), (2-biphenyl)di-tert-butyolphosphine (17mg, 57.6$\mu$mol) and sodium carbonate (46mg, 0.432mmol) were mixed in DMF (6ml) and degassed with argon for 30mins. The mixture was then heated in a microwave for 5mins at 65°C (75W). The DMF was then removed in vacuo and the residue was purified by column
chromatography eluting with 1:1 hexane:CH₂Cl₂ to yield the pure product as a red solid (24mg, 20%), \(R_f = 0.61\) (CH₂Cl₂).

\(^1\)H-NMR [400MHz, CDCl₃] \(\delta\) 1.33 (10H, m, CH₂’s), 1.48 (4H, m, CH₂’s), 1.81 (4H, m, CH₂’s), 4.04 (2H, t, CH₂OPh, \(J = 6.60\)Hz), 4.36 (2H, t, CH₂O, \(J = 6.78\)Hz), 6.56 (2H, m, Py-H), 6.98 (4H, m, Py-H + Ph-H), 7.31 (2H, d, Ph-H, \(J = 8.61\)Hz), 7.63 (2H, d, Ph-H, \(J = 8.61\)Hz), 7.67 (4H, d, Ph-H, \(J = 8.43\)Hz), 7.73 (4H, 2 x d, Ph-H), 7.78 (2H, d, Ph-H, \(J = 8.43\)Hz), 7.96 (2H, m, Py-H), 8.16 (4H, 2 x d, Ph-H).

\(^{13}\)C-NMR [100MHz, CDCl₃] \(\delta\) 25.98, 26.03, 28.7, 29.1, 29.27, 29.33, 29.5, 65.3, 68.3, 111.0, 114.3, 118.7, 121.2, 122.6, 127.1, 127.3, 128.3, 130.3, 131.2, 131.5, 132.3, 132.7, 133.5, 134.9, 136.7, 144.3, 144.9, 151.6, 163.7, 166.4.

\(^{11}\)B-NMR [128.3MHz, CDCl₃] \(\delta\) -0.4891.

HRMS (ESI) = calc. 873.4002, found 873.4003 (M + NH₄⁺).

**Compound 2:**

\(B\) (60mg, 0.133mmol), \(G\) (101mg, 0.160mmol), dibenzylideneacetone palladium (II) (36mg, 39.5μmol), (2-biphenyl)di-tert-butylphosphine (16mg, 53.2μmol) and potassium carbonate (55mg, 0.399mmol) were mixed in DMF (6ml) and degassed with argon for 30mins. The mixture was then heated in a microwave for 5mins at 65°C (75W). The DMF was then removed in vacuo and the residue was subjected column chromatography eluting with 0.5:99.5 EtOAc:toluene. The residue was precipitated from CH₂Cl₂ with cold MeOH to yield the pure product as a bright orange solid (59mg, 49%), \(R_f = 0.21\) (toluene).

\(^1\)H-NMR [400MHz, CDCl₃] \(\delta\) 1.34 (10H, m, CH₂’s), 1.44 (6H, s, 2 x CH₃), 1.49 (4H, m, CH₂’s), 1.81 (4H, m, CH₂’s), 2.57 (6H, s, 2 x CH₃), 4.05 (2H, t, CH₂OPh, \(J = 6.57\)Hz), 4.36 (2H, t, CH₂O, \(J = 6.72\)Hz), 6.00 (2H, s, Py-H), 6.98 (2H, d, Ph-H, \(J = 8.76\)Hz), 7.32
(2H, d, Ph-H, $J = 8.76$Hz), 7.39 (2H, d, Ph-H, $J = 8.13$Hz), 7.63 (2H, d, Ph-H, $J = 8.76$Hz), 7.69 (2H, d, Ph-H, $J = 8.44$Hz), 7.75 (6H, m, Ph-H), 8.15 (4H, dd, Ph-H).

$^{13}$C-NMR [100MHz, CDCl$_3$] $\delta$ 14.6, 26.00, 26.05, 28.8, 29.1, 29.3, 29.4, 29.5, 53.4, 65.3, 68.4, 111.0, 114.4, 118.9, 121.2, 121.3, 122.6, 127.0, 127.7, 127.8, 128.4, 128.8, 129.8, 130.2, 132.4, 132.7, 134.9, 136.7, 140.6, 143.0, 144.3, 151.6, 155.7, 163.7, 164.8, 166.4.

$^{11}$B-NMR [128.3MHz, CDCl$_3$] $\delta$ -0.1836

HRMS (ESI) = calc. 892.4301, found 892.4274 (M – F).

**Compound 3:**

C (60mg, 0.119mmol), G (90mg, 0.143mmol), dibenzylideneacetone palladium (II) (33mg, 35.7$\mu$mol), (2-biphenyl)di-tert-butylphosphine (14mg, 47.6$\mu$mol) and potassium carbonate (49mg, 0.357mmol) were mixed in DMF (6ml) and degassed with argon for 30mins. The mixture was then heated in a microwave for 5mins at 65°C (75W). The DMF was then removed *in vacuo* and the residue was subjected to column chromatography eluting with 2:98 EtOAc:toluene. The residue was precipitated from CH$_2$Cl$_2$ with cold MeOH to yield the pure product as a bright red solid (48mg, 42%), m.p. 192-194°C, $R_f$ = 0.19 (toluene).

$^1$H-NMR [400MHz, CDCl$_3$] $\delta$ 0.97 (6H, t, 2 x CH$_3$CH$_2$), 1.33 (16H, m, CH$_2$’s + 2 x CH$_3$), 1.48 (4H, m, CH$_2$’s), 1.80 (4H, m, CH$_2$’s), 2.29 (4H, q, CH$_2$CH$_3$, $J = 7.50$Hz), 2.53 (6H, s, 2 x CH$_3$), 4.04 (2H, t, CH$_2$OPh, $J = 6.57$Hz), 4.35 (2H, t, CH$_2$O, $J = 6.73$Hz), 6.97 (2H, d, Ph-H, $J = 8.76$Hz), 7.31 (2H, d, Ph-H, $J = 8.44$Hz), 7.38 (2H, d, Ph-H, $J = 8.44$Hz), 7.62 (2H, d, Ph-H, $J = 8.76$Hz), 7.67 (2H, d, Ph-H, $J = 8.44$Hz), 7.73 (6H, m, Ph-H), 8.14 (4H, 2 x d, Ph-H).
13C-NMR [100MHz, CDCl3] δ 11.9, 12.5, 14.6, 17.1, 26.00, 26.03, 28.7, 29.2, 29.3, 29.5, 65.2, 68.4, 114.4, 121.2, 122.6, 127.0, 127.7, 128.3, 129.1, 130.2, 132.4, 132.7, 136.6, 138.3, 140.3, 144.4, 144.8, 151.6, 153.9, 163.7.

11B-NMR [128.3MHz, CDCl3] δ 0.0000

HRMS (ESI) = calc. 990.4809, found 900.4798 (M + Na+).

**Compound 4:**

H (101mg, 0.141mmol), Pd(PPh3)2Cl2 (29mg, 0.041mmol), Cu(I)I (8mg, 0.041mmol) and triethylamine (1ml) were mixed in DMF (4ml) and the mixture was degassed with argon for 30mins. D (40mg, 0.137mmol) in DMF (1.5ml) was added to the initial mixture and the resulting mixture was then heated in a microwave at 65°C (75W) for 5mins. The DMF was then removed *in vacuo* and the residue purified by column chromatography eluting with 2% EtOAc:toluene to yield an orange solid which was then precipitated from dichloromethane with cold methanol to yield the pure product as a bright orange solid (44mg, 36%), Rf = 0.11 (toluene).

1H-NMR [400MHz, CDCl3] δ 1.33 (10H, m, CH2’s), 1.45 (4H, m, CH2’s), 1.82 (4H, m, CH2’s), 4.06 (2H, t, CH2OPh, J = 6.57Hz), 4.34 (2H, t, CH2O, J = 6.72Hz), 6.57 (2H, m, Py-H), 6.94 (2H, m, Ph-H), 6.98 (2H, d, Ph-H, J = 8.76Hz), 7.32 (2H, d, Ph-H, J = 8.76Hz), 7.58 (2H, d, Ph-H, J = 8.44Hz), 7.63 (4H, d, Ph-H, J = 8.44Hz), 7.70 (6H, m, Ph-H), 7.96 (2H, m, Ph-H), 8.06 (2H, d, Ph-H, J = 8.76Hz), 8.15 (2H, d, Ph-H, J = 9.07Hz).

13C-NMR [100MHz, CDCl3] δ 26.00, 26.03, 28.7, 29.3, 29.4, 29.5, 65.4, 68.4, 91.0, 91.3, 111.0, 114.4, 118.8, 121.2, 122.6, 127.2, 127.7, 128.4, 129.6, 130.4, 130.6, 131.4, 131.6, 131.7, 132.4, 132.7, 134.0, 144.5, 144.9, 151.6, 163.7, 164.8, 166.0.

11B-NMR [128.3MHz, CDCl3] δ -0.67.
HRMS (ESI) = calc. 897.4002, found 897.4001 (M + NH$_4^+$).

**Compound 5:**

H (106mg, 0.148mmol), Pd(PPh$_3$)$_2$Cl$_2$ (30mg, 43.2μmol), Cu(I)I (8mg, 43.2μmol) and triethylamine (1ml) were mixed in DMF (4ml) and the mixture was degassed with argon for 30mins. E (50mg, 0.144mmol) in DMF (1.5ml) was added to the initial mixture and the resulting mixture was then heated in a microwave at 65°C (75W) for 5mins. The DMF was then removed *in vacuo* and the residue subjected to column chromatography eluting with 1:99 EtOAc:toluene to yield an orange solid which was then precipitated from dichloromethane with cold methanol to yield the pure product as a bright orange solid (51mg, 38%), m.p. 199-200°C, \( R_f = 0.47 \) (5:95 EtOAc:toluene).

$^1$H-NMR [400MHz, CDCl$_3$] \( \delta \) 1.33 (10H, m, CH$_2$’s), 1.43 (6H, s, 2 x CH$_3$), 1.46 (4H, m, CH$_2$’s), 1.80 (4H, m, CH$_2$’s), 2.56 (6H, s, 2 x CH$_3$), 4.05 (2H, t, CH$_2$OPh, \( J = 6.51\text{Hz} \)), 4.34 (2H, t, CH$_2$O, \( J = 6.69\text{Hz} \)), 5.99 (2H, s, Py-H), 6.99 (2H, d, Ph-H, \( J = 8.80\text{Hz} \)), 7.32 (4H, m, Ph-H), 7.63 (4H, m, Ph-H), 7.68 (4H, 2 x d, Ph-H), 7.74 (2H, d, Ph-H, \( J = 8.25\text{Hz} \)), 8.01 (2H, d, Ph-H, \( J = 8.06\text{Hz} \)), 8.16 (2H, d, Ph-H, \( J = 8.80\text{Hz} \)).

$^{13}$C-NMR [100MHz, CDCl$_3$] \( \delta \) 14.6, 25.97, 26.01, 28.7, 29.2, 29.3, 29.5, 65.4, 68.3, 90.0, 91.4, 110.9, 114.3, 118.9, 121.2, 121.4, 122.6, 123.5, 127.4, 127.7, 128.3, 129.6, 130.2, 131.5, 132.3, 132.4, 132.7, 136.7, 142.9, 144.9, 151.6, 155.8, 163.7, 166.0.

$^{11}$B-NMR [128.3MHz, CDCl$_3$] \( \delta \) -0.2446.

HRMS (ESI) = calc. 958.4183, found 958.4174 (M + Na$^+$).
Compound 6:

H (88mg, 0.128mmol), Pd(PPh$_3$)$_2$Cl$_2$ (26mg, 37.2μmol), Cu(I)I (7.2mg, 37.2μmol) and triethylamine (1ml) were mixed in DMF (4ml) and degassed with argon for 30mins. F (50mg, 0.124mmol) in DMF (1ml) was then added to this solution and the mixture was then heated in a microwave at 65°C (75W) for 5mins. The DMF was then removed in vacuo and the residue purified by column chromatography eluting with 0-2% EtOAc:toluene to yield an orange solid which was then precipitated from dichloromethane with cold methanol to yield the pure product as a bright red solid (45mg, 38%), m.p. 184-185°C, $R_f$ = 0.4 (toluene).

$^1$H-NMR [400MHz, CDCl$_3$] δ 0.96 (6H, t, CH$_3$CH$_2$, $J = 7.51$Hz), 1.31 (16H, m, CH$_2$’s + 2 x CH$_3$), 1.44 (4H, m, CH$_2$’s), 1.79 (4H, m, CH$_2$’s), 2.27 (4H, q, CH$_2$CH$_3$, $J = 7.50$Hz), 2.52 (6H, s, 2 x CH$_3$), 4.03 (4H, t, CH$_2$OPh, $J = 6.57$Hz), 4.32 (4H, t, CH$_2$O, $J = 6.73$Hz), 6.97 (2H, d, Ph-H, $J = 9.07$Hz), 7.30 (4H, m, Ph-H), 7.63 (8H, m, Ph-H), 7.71 (2H, d, Ph-H, $J = 8.76$Hz), 8.03 (2H, d, Ph-H, $J = 8.76$Hz), 8.14 (2H, d, Ph-H, $J = 9.07$Hz).

$^{13}$C-NMR [100MHz, CDCl$_3$] δ 11.2, 11.9, 13.9, 16.4, 25.3, 28.0, 28.0, 28.4, 28.6, 28.7, 28.8, 64.7, 67.7, 89.2, 90.8, 110.3, 113.7, 120.5, 121.9, 122.7, 127.0, 127.7, 128.0, 128.9, 129.5, 130.9, 131.7, 132.0, 132.3, 135.7, 137.5, 150.9, 163.1, 164.2, 165.3.

$^{11}$B-NMR [128.3MHz, CDCl$_3$] δ -0.1836.

HRMS (ESI) = calc. 1009.5256, found 1009.5259 (M + NH$_4^+$).
**S2: DSC thermograms for compounds 1, 2 and 4**

**Compound 1:**

![Graph showing DSC thermogram for Compound 1]
Compound 2:
Compound 4:
S3: $^1$H-NMR spectra for mesogenic BODIPYs (compounds 1-6)

$^1$H-NMR spectrum for compound 1:
$^1$H-NMR spectrum for compound 2:
$^1$H-NMR spectrum for compound 3:
1H-NMR spectrum for compound 4:
$^1$H-NMR spectrum for compound 5:
$^1$H-NMR spectrum for compound 6:
**S4: HRMS profiles for compounds 1-6**

**HRMS (ESI) for compound 1:**

![HRMS profile for compound 1](image)

**Theoretical Isotope Model: [M + NH₄]⁺**

**Observed Data**
HRMS (ESI) for compound 2:

Theoretical Isotope Model: \([M - F]^+\)

Observed Data
HRMS (ESI) for compound 3:

Theoretical Isotope Model: [M + Na]⁺

Observed Data
HRMS (ESI) for compound 4:
HRMS (ESI) for compound 5:
HRMS (ESI) for compound 6:

Theoretical Isotope Model: [M + NH4]⁺

Observed Data
S5: HPLC traces for compounds 1-6

HPLC trace for compound 1 (4:1 MeCN:CH₂Cl₂):
HPLC trace for compound 2 (4:1 MeCN:CH₂Cl₂):
HPLC trace for compound 3 (4:1 MeCN:CH₂Cl₂):
HPLC trace for compound 4 (4:1 MeCN:CH₂Cl₂):
HPLC trace for compound 5 (4:1 MeCN:CH₂Cl₂):
HPLC trace for compound 6 (9:1 MeCN:CH₂Cl₂):