Polyfluorenes Without Monoalkylfluorene Defects

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Summary of the relevant literature

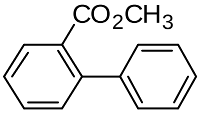
Reviews of light-emitting polymers.[1-6]

A number of approaches have been adopted to achieve stable blue emission from polyfluorenes including copolymerisation with anthracene,[7] attachment of aryl groups in place of alkyl substituents,[8-10] blending with triarylamines,[11] and treatment of the monomers with base to attempt to remove any monoalkylated material.[12] Attachment of dendrimers,[13] introduction of twisted biphenyls,[14,15] use of triarylamine end groups,[16] or electron-deficient end groups[17] and incorporation of adamantanes[18] have also been employed with success. Extensive studies of model materials carrying a fluorenone unit have supported the case for this unit being responsible for the long wavelength emission in polyfluorenes.[19-22]

General methods

$^{13}C\{^1H\}$ NMR spectra were recorded on Varian Inova 500 or Varian Inova 400 instruments using $CDCl_3$ as an internal deuterium lock. IR spectra were recorded on a Perkin Elmer Spectrum One FT-IR Spectrometer. UV-Vis spectra were recorded using a Cary Bio 8G spectrometer. Photoluminescence spectra were recorded on Varian Cary Eclipse Fluorescence Spectrometer. Thin films were prepared from toluene solution (15 mg/mL) on cut microscope slides with a Cammax Precima spin-coater at 2000 rpm for 1 min. Melting points were determined using Büchi 510 melting point apparatus, and are uncorrected. Accurate mass spectra were recorded at CSIRO Molecular and Health Technologies on a ThermoQuest MAT95 high resolution mass spectrometer, employing 70 eV electron energy. Gel Permeation Chromatography measurements were performed at CSIRO Molecular and Health Technologies using a Waters 717plus autosampler, Waters 515 HPLC pump and a Waters 2414 refractive index detector. A 100 µL injection was used and samples were passed through three 30 cm, PL gel (5 µm) mixed C columns and one 30 cm, PL gel (3 µm) mixed E column at 1 cm^3 min^{-1} with THF as solvent. Molar masses are calculated relative to polystyrene standards. Thermogravimetric analysis was carried out on a Perkin Elmer Pyris 1 Thermogravimetric Analyzer. Differential scanning calorimetric measurements were measured on a Perkin Elmer Sappire Differential Scanning Calorimeter. Column chromatography was carried out on silica gel [Merck Kieselgel 60 (230-430 mesh)]. TLC was performed on 0.25 nm thick plates precoated with Merck Kieselgel 60 F_{254} silica gel, and visualized by UV light (254 and 366 nm) or by developing with an aqueous cerium(VI) solution. Reagents and solvents were used as obtained from commercial suppliers except where indicated otherwise.

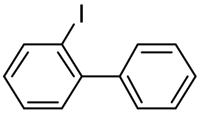
2-Carbomethoxybiphenyl (1)



A mixture of biphenyl-2-carboxylic acid (10 g, 50.5 mmol), conc. sulphuric acid (50 mg, 0.5 mmol) and methanol (200 cm^3) was heated at reflux for 20 hours. The solvent was evaporated under reduced pressure to give a crude oil. The residue was dissolved in petroleum ether 40-60 °C and filtered. The organic phase was extracted with aqueous sodium bicarbonate solution (10%; 3×30 cm^3), and water (3×30 cm^3) and then dried over magnesium sulphate and evaporated under reduced pressure. The crude was distilled using Kugelrohr distillation apparatus (100 mmHg, 100-110 °C) to give the *title compound* as colourless liquid (6.3 g, 59 %).

^{1}H NMR (500 MHz; $CDCl_3$) *d* 3.65 (3 H, s), 7.34-7.44 (7 H, m), 7.54 (1 H, dd, *J* = 8, 8), 7.85 (1 H, d, *J* = 8); ^{13}C NMR (125 MHz; $CDCl_3$) *d* 51.9, 127.0, 127.1, 127.9, 128.2, 129.7, 130.6, 130.8, 131.2, 141.2, 142.4, 169.1; The d_H and d_C data are in agreement with the literature values.[23]

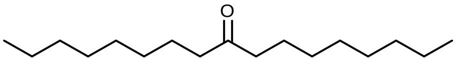
2-Iodobiphenyl[24] (3)



2-Aminobiphenyl (10 g, 59.1 mmol) was added slowly to a stirred mixture of conc. hydrochloric acid (35.4%; 27 cm^3, 76.8 mmol) and water (100 cm^3). Aqueous sodium nitrite solution (20%; 22.4 g, 65 mmol) was added to the mixture below 5 °C for 20 min and stirred for 1 h at the same temperature. The mixture was added to an aqueous solution of KI (11.9 g, 118.2 mmol) in water (100 cm^3) slowly and stirred overnight at room temperature. Diethyl ether (100 cm^3) was added to the mixture and the organic phase was separated. The aqueous phase was extracted with diethyl ether (3×100 cm^3). The combined organic phases were dried over magnesium sulphate. The solvent was evaporated under reduced pressure and purified by column chromatography (petroleum ether 40-60 °C only). The crude product was dissolved in dichloromethane (100 cm^3) and treated with aqueous sodium hydroxide (33 %; 50 cm^3) to decolorize. The organic layer was isolated and dried over magnesium sulphate. The resultant solution was evaporated under reduced pressure and purified by column chromatography (petroleum ether 40-60 °C only) to give the *title compound* as colourless liquid (14.5 g, 88 %).

^{1}H NMR (500 MHz; $CDCl_3$) *d* 7.06 (1 H, ddd, *J* = 8, 8, 2), 7.32-7.43 (3 H, m), 7.41-7.47 (4H, m), 7.98 (1 H, dd, *J* = 8, 2); ^{13}C NMR (125 MHz; $CDCl_3$) *d* 98.6, 127.6, 127.9, 128.1, 128.7, 129.2, 130.0, 139.4, 144.1, 146.5. The d_H and d_C data are in agreement with the literature values.[24]

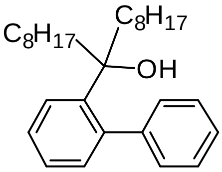
9-Heptadecanone[25] (4)



To a suspension of $AlCl_3$ (4 g, 30.0 mmol) in dichloromethane (35 cm^3) was added nonanoic chloride (5.4 cm^3, 30 mmol) at –78 °C over 10 min under nitrogen. The mixture was allowed to warm up to room temperature and stirred for 1 h. The mixture was cooled down to –78 °C before trioctyl aluminium (25% in hexane; 26.4 cm^3, 12.1 mmol) was added. The mixture was allowed to warm up to room temperature and stirred overnight before being quenched with water (30 cm^3). The organic phase was separated and the aqueous phase extracted with diethyl ether (2×20 cm^3). The combined organic phases were washed with aqueous sodium bicarbonate solution (15%, 3×30 cm^3) and water (2×30 cm^3) before being dried over magnesium sulphate. After removal of the solvent under reduced pressure, the residue was purified by column chromatography (dichloromethane:petroleum ether 40-60 °C = 1:4) on silica gel and recrystallised from ethanol to give the *title compound* as white solid (5.1 g, 67 %).

m.p. 50 °C (lit.,[26] 50 °C); ^{1}H NMR (500 MHz; $CDCl_3$) *d* 0.86 (6 H, t, *J* = 7) 1.24-1.27 (20 H, m), 1.52-1.55 (4 H, m), 2.36 (4 H, t, *J* = 7); ^{13}C NMR (125 MHz; $CDCl_3$) *d* 14.1, 22.6, 23.8, 29.1, 29.2, 29.4, 31.8, 42.8, 211.8. The d_H and d_C data are in agreement with the literature values.[26]

9-Biphen-2-yl-heptadecan-9-ol (2a)

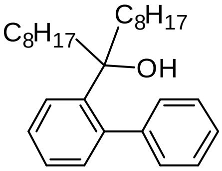


(Route 1, Scheme 1)

1-Bromooctane (14.5 cm^3, 82.9 mmol) was added slowly to a mixture of magnesium (3.0 g, 0.12 mol) and dry diethyl ether (50 cm^3) for 30 min to keep the mixture at a gentle reflux. The mixture was then stirred for 2 h at room temperature. 2-Carbomethoxybiphenyl **1** (4.0 g, 18.9 mmol) was dissolved in a separate flask in dry diethyl ether (50 cm^3) and the resultant Grignard reagent was transferred via syringe to the mixture at 0 °C. The mixture was stirred overnight at room temperature before being quenched with aqueous ammonium chloride solution (10%; 5 cm^3) and water (10 cm^3) at 0 °C. The organic phase was separated and the aqueous phase was extracted with ether (2×20 cm^3). The combined organic phases were dried over magnesium sulphate before being evaporated under reduced pressure to give the crude oil. The crude oil was purified by column chromatography (petroleum ether 40-60 °C:dichloromethane = 7:3) on silica gel to give the *title compound* as a colourless oil (2.8 g, 36 %).

Anal. Calcd. for $C_{29}H_{44}O$: C, 85.2; H, 10.9. Found: C, 85.3; H, 11.0. IR (neat liquid) 3479, 2955, 2923, 2856, 1466, 1443, 1377, 1072, 1009, 915, 758, 704 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$) *d* 0.90 (6 H, t, *J* = 7) 1.01-1.34 (24 H, m), 1.54-1.60 (2 H, m) 1.62 (1 H, br s), 1.68-1.74 (2 H, m), 7.06 (1 H, dd, *J* = 8, 1) 7.22-7.28 (3 H, m), 7.35-7.40 (4 H, m), 7.58 (1 H, dd, *J* = 8, 1); ^{13}C NMR (125 MHz; $CDCl_3$) *d* 14.1, 22.6, 23.7, 29.3, 29.5, 29.9, 31.8, 43.2, 78.8, 125.5, 126.9, 127.1, 127.1, 127.5, 129.0, 131.9, 139.9, 143.1, 143.9; MS (EI) *m/z* (rel intensity) 407.3 [2, $(M-H)^+$], 390.3 [57], 295.2 [100], 277.2 [18], 179.1 [69], 165.0 [64], 57.1 [34]; HRMS (EI) *m/z* 407.3292 (407.3308 calcd for $[M-H]^+$ $C_{29}H_{43}O$).

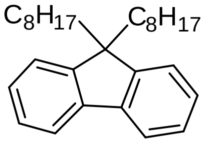
9-Biphen-2-yl-heptadecan-9-ol (2b)



(Route 2, Scheme 1)

n-Butyllithium (2.5 M in hexane, 4.3 cm^3, 10.7 mmol) was added slowly to the mixture of 2-iodobiphenyl **3** (3.0 g, 10.7 mmol) and dry tetrahydrofuran (150 cm^3) at –78 °C over 20 min under nitrogen. The mixture was stirred for 2 h at the same temperature. 9-Heptadecanone **4** (2.5 g, 9.6 mmol) was dissolved in dry tetrahydrofuran (50 cm^3) in a separate flask under nitrogen. The 9-heptadecanone **4** solution was added via syringe to the mixture slowly over 20 min at –78 °C and stirred overnight at room temperature. The reaction was quenched with an aqueous ammonium chloride solution (10%; 5 cm^3) and water (30 cm^3) at 0 °C. The organic phase was separated and the aqueous phase was extracted with dichloromethane (20 cm^3). The combined organic phases were evaporated under reduced pressure to give the *title compound* as a crude oil (3.9 g). The crude product was used in the next step without further purification.

9,9-Dioctyl-9*H*-fluorene (5a)



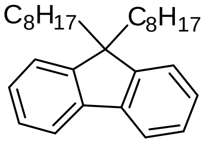
(Route 1, Scheme 1)

Other examples of alkylative cyclization to form fluorenes and derivatives have been reported.[27-31]

To a solution of 9-biphenyl-2-yl-heptadecan-9-ol **2a** (2.7 g, 6.6 mmol) in dichloromethane (50 cm^3) was added trifluoroboron etherate (0.84 cm^3, 6.6 mmol) slowly via syringe and the solution was stirred overnight at room temperature. The reaction was quenched with methanol (2 cm^3) and evaporated under reduced pressure to give a crude oil. The crude oil was purified by column chromatography (petroleum ether 40-60 °C only) to give the *title compound* as a colourless oil (2.5 g, 97 %).

^{1}H NMR (500 MHz; $CDCl_3$) *d* 0.64-0.67 (4 H, m), 0.85 (6 H, t, *J* = 7) 1.07-1.24 (20 H, m), 1.96-2.00 (4 H, m), 7.29-7.37 (6 H, m), 7.72-7.73 (2 H, m); ^{13}C NMR (125 MHz; $CDCl_3$) *d* 14.1, 22.6, 23.7, 29.2, 29.2, 30.0, 31.8, 40.4, 54.9, 119.6, 122.8, 126.6, 126.9, 141.0, 150.6. The d_H and d_C data are in agreement with the literature values.[32]

9,9-Dioctyl-9*H*-fluorene (5b)

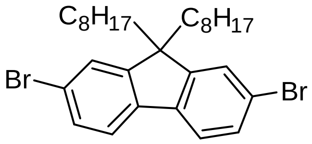


(Route 2, Scheme 1)

The crude product **2b** (3.2 g) of the previous step was dissolved in dichloromethane (50 cm^3). Boron trifluoride diethyl etherate (1.2 cm^3, 9.6 mmol) was added to the mixture slowly and stirred overnight at room temperature. The reaction was quenched with methanol (2 cm^3) and evaporated under reduced pressure to give a crude oil. The crude oil was purified by column chromatography (petroleum ether 40-60 °C only) to give the *title compound* as a colourless oil (3 g, 80 %).

^{1}H NMR (500 MHz; $CDCl_3$) *d* 0.64-0.67 (4 H, m), 0.85 (6 H, t, *J* = 7) 1.07-1.24 (20 H, m), 1.96-2.00 (4 H, m), 7.29-7.37 (6 H, m), 7.72-7.73 (2 H, m); ^{13}C NMR (125 MHz; $CDCl_3$) *d* 14.1, 22.6, 23.7, 29.2, 29.2, 30.0, 31.8, 40.4, 54.9, 119.6, 122.8, 126.6, 126.9, 141.0, 150.6. The d_H and d_C data are in agreement with the literature values.[32]

2,7-Dibromo-9,9-dioctyl-9*H*-fluorene (6a, 6b)

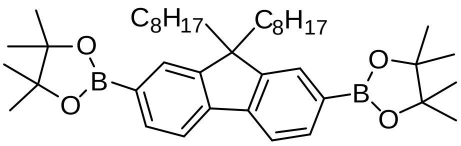


Bromine (0.7 cm^3, 13.8 mmol) was added slowly to a mixture of 9,9-dioctyl-9*H*-fluorene **5a**, **5b** (2.7 g, 6.9 mmol), iodine (140.0 mg, 0.1 mmol) and dichloromethane (70 cm^3) over 30 min at 0 °C in the dark. The mixture was stirred at 0 °C for 1 h then at room temperature for 2 h. An aqueous $Na_2S_2O_3$ solution (10%, 5 cm^3) and then water (30 cm^3) were added to quench the reaction. The organic phase was separated and the aqueous phase was extracted with dichloromethane. The combined organic phases were dried over magnesium sulphate and evaporated under reduced pressure to give a crude solid. The crude material was purified by column chromatography (petroleum ether 40-60 °C only) and recrystallised from ethanol to give the *title compound* (2.8 g, 74 %) as colourless crystals.

mp 53-54 °C (ethanol) [lit.,[33] 51-54 °C (hexane)]; ^{1}H NMR (500 MHz; $CDCl_3$) *d* 0.54-0.64 (4 H, m), 0.83 (6 H, t, *J* = 7) 1.04-1.28 (20 H, m), 1.88-1.93 (4 H, m), 7.43-7.47 (4

H, m), 7.52 (2 H, d, *J* = 8); ^{13}C NMR (125 MHz; CDCl$_3$) *d* 14.0, 22.6, 23.7, 29.1, 29.2, 29.9, 31.8, 40.2, 55.7, 121.0, 121.5, 126.2, 130.2, 139.1, 152.6. The d_{H} and d_{C} data are in agreement with the literature values.[32]

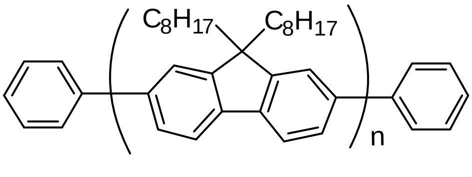
9,9-Dioctyl-2,7-bis(4,4',5,5'-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-fluorene (7b)



n-Butyllithium (2.5 M in hexane; 2.4 cm^3, 6.0 mmol) was added slowly over 30 min to a stirred solution of 2,7-dibromo-9,9-dioctyl-9*H*-fluorene **6b** (1.5 g, 2.7 mmol) in dry tetrahydrofuran (70 cm^3) at –78 °C. The mixture was stirred for 1 h at the same temperature before 2-isopropoxy-4,4',5,5'-tetramethyl-1,3,2-dioxaborolane (2.0 cm^3, 9.8 mmol) was added slowly over 30 min. The mixture was allowed to warm up slowly to room temperature while it was stirred overnight. The reaction was quenched with water (10 cm^3) and the solvent was evaporated under reduced pressure. The residue was dissolved in dichloromethane (50 cm^3) and water (20 cm^3) and the aqueous phase was extracted with dichloromethane (2×20 cm^3). The combined organic phases were dried over magnesium sulphate and evaporated under reduced pressure. The crude product was purified by column chromatography (petroleum ether 40-60 °C : dichloromethane=3:7) and recrystallised from acetone to give the *title compound* as colourless crystals (1.0 g, 57 %).

mp 129 °C (acetone) (lit.,[34] 127-128 °C (heptane)); ^{1}H NMR (500 MHz; $CDCl_3$) *d* 0.50-0.60 (4 H, m), 0.81 (6 H, t, *J* = 7) 0.96-1.23 (20 H, m), 1.39 (24 H, s), 1.95-2.05 (4 H, m), 7.72 (2H, d, *J* = 8), 7.75 (2 H, s), 7.81 (2 H, dd, *J* = 8, 1); ^{13}C NMR (125 MHz; $CDCl_3$) *d* 14.0, 22.6, 23.6, 24.9, 29.1, 29.2, 29.9, 31.8, 40.0, 55.2, 83.7, 119.3, 119.4, 128.8, 133.5, 143.8, 150.4. The d_H and d_C data are in agreement with the literature values.[35]

a,? -Bis(phenyl)poly(9,9-dioctyl-9*H*-fluorene-2,7-diyl) (8a)



Examples of Yamamoto polymerizations to prepare polyfluorenes have been previously reported.[36,37]

To a stirred solution of Ni(COD)$_2$ (276 mg, 1.0 mmol) and 2,2'-bipyridine(157 mg, 1.0 mmol) in dry dimethylformamide (3.5 cm^3) was added COD (123 µm^3, 1.0 mmol) and the resultant solution was stirred for 1 h at 75 °C under nitrogen. 2,7-Dibromo-9,9-dioctyl-9*H*-fluorene **6a** (0.5 g, 0.91 mmol) was dissolved in toluene (6 cm^3) in a separate flask under nitrogen and then added to the mixture. The mixture was stirred overnight for 24 h at 75 °C under nitrogen. Bromobenzene (83 µm^3, 0.91 mmol) was added to the mixture and stirred for 12 h under the same conditions. The mixture was dropped slowly by pipette into a stirred solvent mixture (methanol:acetone:con. HCl = 1:1:1; 150 cm^3) and the resultant mixture was stirred for 2 h. The precipitate was filtered and washed with the solvent mixture (methanol:acetone:con. HCl = 1:1:1; 50 cm^3). The precipitate was dissolved in the minimum amount of chloroform and added slowly to a vigorously stirred solution of methanol (100 cm^3) to give a fibrous precipitate. The mixture was filtered and washed with methanol (50 cm^3). The precipitate was dried under high vacuum to give the *title compound* as light green fibres (320 mg, 90 %)

Anal. Calcd. for polymer: C, 89.6; H, 10.4. Found: C, 89.3; H, 10.9. IR (neat solid) 2923, 2852, 1458, 1404, 1377, 1255, 1000, 885, 812, 757, 735 cm^{-1}; ^{1}H NMR (500

MHz; $CDCl_3$) *d* 0.7-1.0 (br m, CH_2+CH_3) 1.0-1.3 (br m, CH_2), 1.9-2.3 (br m, CH_2), 7.5-8.0 (br m, Ar*H*); ^{13}C NMR (125 MHz; $CDCl_3$) *d* 14.1, 22.6, 23.9, 29.2, 29.2, 30.0, 31.8, 40.4, 55.8, 120.0, 121.5, 126.1, 140.0, 140.5, 151.8; GPC assay in tetrahydrofuran vs. narrow polystyrene standards revealed M_w = 37,400, M_n = 21,700, M_p = 29,400, PDI = 1.7;

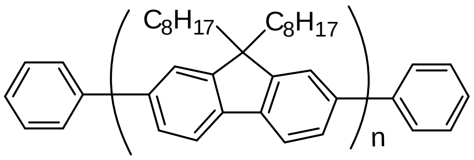
Polymer **8b** was synthesised by the same method as **8a** using 9,9-dioctyl-9*H*-fluorene **6b** to give the *title compound* as light green fibres (300 mg, 85 %).

Anal. Calcd. for polymer: C, 89.6; H, 10.4. Found: C, 89.4; H, 10.5. IR (neat solid) 2923, 2851, 1457, 1402, 1376, 1252, 999, 885, 812, 757, 733 cm^{-1}; ^{1}H NMR (500 MHz; $CDCl_3$) *d* 0.7-1.0 (br m, CH_2+CH_3) 1.0-1.3 (br m, CH_2), 1.9-2.3 (br m, CH_2), 7.5-8.0 (br m, Ar*H*); ^{13}C NMR (125 MHz; $CDCl_3$) *d* 14.1, 22.6, 23.9, 29.2, 29.2, 30.0, 31.8, 40.4, 55.3, 120.0, 121.5, 126.1, 140.0, 140.5, 151.8; GPC assay in tetrahydrofuran vs. narrow polystyrene standards revealed M_w = 25,000, M_n = 9,800, M_p = 27,000, PDI = 2.6;

Polymer **8c** was synthesised by the same method as **8a** using conventional 9,9-dioctyl-9*H*-fluorene[38,39] **6c** to give the *title compound* as light green fibres (280 mg, 79 %).

Anal. Calcd. for polymer: C, 89.6; H, 10.4. Found: C, 89.1; H, 10.9. IR (neat solid) 2954, 2923, 2852, 1458, 1404, 1377, 1254, 1000, 885, 812, 757, 721 cm^{-1}; ^{1}H NMR (500 MHz; CDCl$_3$) ***d*** 0.7-1.0 (br m, CH_2+CH_3) 1.0-1.3 (br m, CH_2), 1.9-2.3 (br m, CH_2), 7.5-8.0 (br m, Ar*H*); ^{13}C NMR (125 MHz; CDCl$_3$) ***d*** 14.1, 22.6, 23.9, 29.2, 29.2, 30.0, 31.8, 40.4, 55.3, 120.0, 121.5, 126.1, 140.0, 140.5, 151.8; GPC assay in tetrahydrofuran vs. narrow polystyrene standards revealed M_w = 39,800, M_n = 18,300, M_p = 41,900, PDI = 2.2;

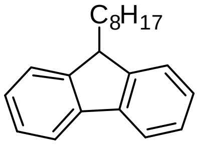
a,? -Bis(phenyl)poly(9,9-dioctyl-9*H*-fluorene-2,7-diyl) (8d)



To a Schlenk tube was added 2,7-dibromo-9,9-dioctyl-9*H*-fluorene **6b** (353 mg, 0.64 mmol), 9,9-dioctyl-2,7-bis(4,4',5,5'-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-fluorene **7b** (414 mg, 0.64 mmol) and tetrakis(triphenylphosphine) palladium (7 mg, 0.04 mmol) under a nitrogen atmosphere. Toluene (15 cm^3) was added to the mixture and the resultant mixture was stirred at 90 °C for 5 min before an aqueous tetraethyl ammonium hydroxide solution (2 cm^3) was added. The mixture was stirred for 24 h at 90 °C under nitrogen. Bromobenzene (0.07 cm^3, mmol) was added to the mixture and stirred at 90 °C for 12 h. Phenylboronic acid (157 mg, 1.29 mmol) was added to the mixture after which the mixture was stirred for 12 h. The mixture was cooled down to room temperature and dropped by pipette into a stirred solution of methanol (100 cm^3) in an open vessel. The precipitate was isolated and dissolved in dichloromethane. The solution was passed through a pad of silica. The collected dichloromethane solution was concentrated under reduced pressure and added dropwise to a vigorously stirred solution of methanol (100 cm^3) in an open vessel. The precipitate was filtered and washed with methanol (50 cm^3) on a filter funnel. The precipitate was dried under high vacuum to give *the title compound* as light green fibres (430 mg, 86 %).

Anal. Calcd. for polymer: C, 89.6; H, 10.4. Found: C, 89.1; H, 10.8. IR (neat solid) 2924, 2852, 1458, 1377, 1275, 1259, 1000, 885, 812, 750 cm^{-1}; ^1H NMR (500 MHz; $CDCl_3$) *d* 0.7-1.0 (br m, CH_2+CH_3) 1.0-1.3 (br m, CH_2), 1.9-2.3 (br m, CH_2), 7.5-8.0 (br m, Ar*H*); ^{13}C NMR (125 MHz; $CDCl_3$) *d* 14.1, 22.6, 23.9, 29.2, 29.2, 30.0, 31.8, 40.4, 55.3, 120.0, 121.5, 126.1, 140.0, 140.5, 151.8; GPC assay in tetrahydrofuran vs. narrow polystyrene standards revealed M_w = 21,100, M_n = 6,000, M_p = 27,200, PDI = 3.5;

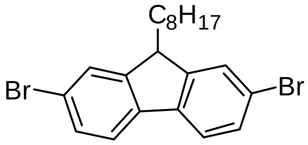
9-Octyl-9*H*-fluorene[35]



A mixture of 9*H*-fluorene (7.0 g, 42.1 mmol), potassium hydroxide (1.2 g, 21.1 mmol) and octan-1-ol (28.5 g, 0.31 mmol) was stirred overnight in a 100 cm^3 Chemware PFA (perfluoroalkoxy) Erlenmeyer flask at 190 ºC. The mixture was cooled to room temperature before being purified by dry flash chromatography (petroleum ether 40-60 °C only) to give the *title compound* as a colourless liquid (10.8 g, 92 %).

^{1}H NMR (500 MHz; CDCl$_3$) *d* 0.95 (3 H, t, *J* = 7), 1.23-1.40 (12 H, m), 2.03-2.11 (2 H, m), 4.04 (1 H, t, *J* = 6), 7.34 (2H, ddd, *J* = 7, 7, 1), 7.39 (2H, dd, *J* = 7, 7), 7.55 (2 H, d, *J* = 7), 7.79 (2 H, d, *J* = 7); ^{13}C NMR (125 MHz; CDCl$_3$) *d* 14.0, 22.6, 25.7, 29.3, 29.4, 30.0, 31.8, 33.1, 47.5, 119.7, 124.3, 126.7, 126.8, 141.1, 147.6. The d_{H} and d_{C} data are in agreement with the literature values.[35]

2,7-Dibromo-9-octyl-9*H*-fluorene[35] (9)

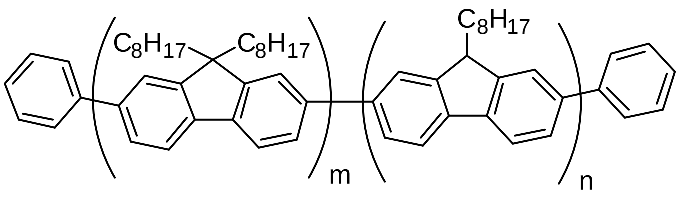


Bromine (1.5 cm^3, 28.7 mmol) was added dropwise over 10 min to a stirred solution of 9-octyl-9*H*-fluorene (4.0 g, 14.4 mmol) and iodine (0.3 g, 1.1 mmol) in dichloromethane (30 cm^3) at 0 ºC in the dark. The mixture was stirred for 0.5 h at the same temperature and then for 2.5 h at room temperature in the dark before it was quenched with an aqueous sodium thiosulfate solution (20%; 5 cm^3). The organic phase was separated, dried over magnesium sulphate and evaporated under reduced pressure. The crude product was recrystallised from ethanol to give the *title compound* as a white solid (4.7 g, 75 %).

mp 77-80 ºC (ethanol) (lit.,[35] 77-80 ºC (ethanol)); ^{1}H NMR (400 MHz; CDCl$_3$) *d* 0.86 (3 H, t, *J* = 7), 1.06-1.35 (12 H, m), 1.90-2.04 (2 H, m), 3.95 (1 H, t, *J* = 6), 7.48 (2 H, dd, *J* = 8, 2), 7.56 (2 H, d, *J* = 8), 7.62 (2 H, br s); ^{13}C NMR (100 MHz; CDCl$_3$) *d* 14.1, 22.6, 25.4, 29.2, 29.3, 29.8, 31.8, 32.6, 47.5, 121.1, 121.1, 127.6, 130.2, 139.1, 149.3. The d_H

and d_C data are in agreement with the literature values.[35]

a,? -Bis(phenyl)poly(9,9-dioctyl-9*H*-fluorene-2,7-diyl)-co-(9-dioctyl-9*H*-fluorene-2,7-diyl) (10)



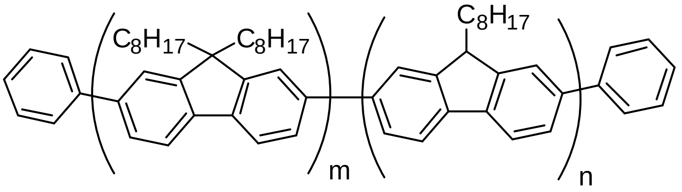
m:m = 99.94:0.06

To a mixture of Ni(COD)$_2$ (276 mg, 1.0 mmol), 2,2'-bipyridine(157 mg, 1.0 mmol) and dry dimethylformamide (3.5 cm^3) was added COD (123 µm^3, 1.0 mmol) and the solution was stirred for 1 h at 75 °C under nitrogen. 2,7-Dibromo-9,9-dioctyl-9*H*-fluorene **6b** (0.5 g, 0.91 mmol) was dissolved in toluene (6 cm^3) in a separate flask under nitrogen and then added to the mixture. 2,7-Dibromo-9-octyl-9*H*-fluorene **9** (0.25 g, 0.57 mmol) was dissolved in toluene (100 cm^3) in a separate flask under nitrogen and 0.1 cm^3 (0.25 mg of **9**, 0.57 µmol) was taken via syringe and added to the mixture. The mixture was stirred overnight for 24 h at 75 °C under nitrogen. Bromobenzene (83 µm^3, 0.91 mmol) was added to the mixture and stirred for 12 h under the same condition. The mixture was poured slowly to the solvent mixture (methanol:acetone:con. HCl = 1:1:1;

150 cm^3) and stirred for 2 h. The mixture was filtered and washed with the solvent mixture (methanol:acetone:con. HCl = 1:1:1; 50 cm^3). The precipitate was dissolved in the minimum amount of chloroform and added slowly to a vigorously stirred solution of methanol (50 cm^3). The precipitate was filtered and washed with methanol (50 cm^3) on filter funnel. The precipitate was dried under high vacuum to give the *title compound* as light green fibres (300 mg, 85 %).

Anal. Calcd. for polymer: C, 89.6; H, 10.4. Found: C, 89.3; H, 10.9. IR (neat solid) 2923, 2852, 1458, 1404, 1377, 1256, 1000, 908, 885, 812, 757, 734 cm^{-1}; ^{1}H NMR (500 MHz; $CDCl_3$) *d* 0.7-1.0 (br m, CH_2+CH_3) 1.0-1.3 (br m, CH_2), 1.9-2.3 (br m, CH_2), 7.5-8.0 (br m, Ar*H*); ^{13}C NMR (125 MHz; $CDCl_3$) *d* 14.1, 22.6, 23.9, 29.2, 29.2, 30.0, 31.8, 40.4, 55.8, 120.0, 121.5, 126.1, 140.0, 140.5, 151.8; GPC assay in tetrahydrofuran vs. narrow polystyrene standards revealed M_w = 71,000, M_n = 38,300, M_p = 68,400, PDI = 1.9;

a,? -Bis(phenyl)poly(9,9-dioctyl-9H-fluorene-2,7-diyl)-co-(9-dioctyl-9H-fluorene-2,7-diyl) (11)



m:m = 99.4:0.6

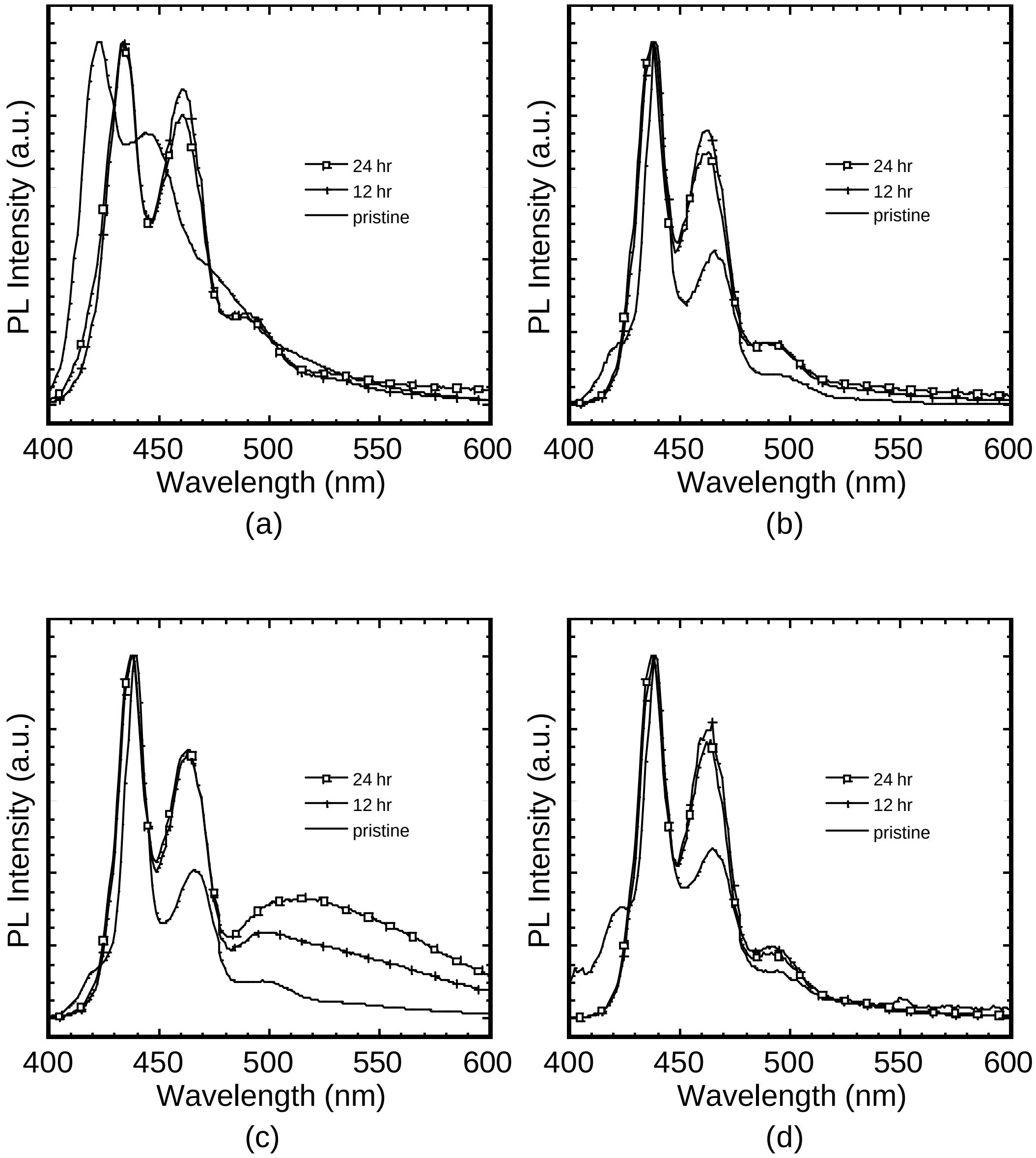
To a mixture of Ni(COD)$_2$ (276 mg, 1.0 mmol), 2,2'-bipyridine(157 mg, 1.0 mmol) and dry dimethlyformamide (3.5 cm^3) was added COD (123 µm^3, 1.0 mmol) and the solution was stirred for 1 h at 75 °C under nitrogen. 2,7-Dibromo-9,9-dioctyl-9*H*-fluorene **6b** (0.5 g, 0.91 mmol) was dissolved in toluene (6 cm^3) in a separate flask under nitrogen then added to the mixture. 2,7-Dibromo-9-octyl-9*H*-fluorene **9** (0.25 g, 0.57 mmol) was dissolved in toluene (100 cm^3) in a separate flask under nitrogen and 1 cm^3 (2.5 mg of **9**, 5.7 µmol) was taken via syringe and added to the mixture. The mixture was stirred overnight for 24 h at 75 °C under nitrogen. Bromobenzene (83 µm^3, 0.91 mmol) was added to the mixture and stirred for 12 h under the same condition. The mixture was poured slowly to the solvent mixture (methanol:acetone:con. HCl = 1:1:1; 150 cm^3) and stirred for 2 h. The mixture was filtered and washed with the solvent mixture (methanol:acetone:con. HCl = 1:1:1; 50 cm^3). The precipitate was dissolved in the minimum amount of chloroform and added slowly to a vigorously stirred solution of methanol (50 cm^3). The precipitate was filtered and washed with methanol (50 cm^3) on filter funnel. The precipitate was dried under high vacuum to give *title compound* as light green fibre (310 mg, 87 %).

Anal. Calcd. for polymer: C, 89.6; H, 10.4. Found: C, 88.8; H, 11.5. IR (neat solid) 2923, 2852, 1458, 1404, 1377, 1259, 1000, 885, 812, 750, 735 cm^{-1}; ^{1}H NMR (500 MHz; $CDCl_3$) ***d*** 0.7-1.0 (br m, CH_2+CH_3) 1.0-1.3 (br m, CH_2), 1.9-2.3 (br m, CH_2), 7.5-8.0 (br m, Ar*H*); ^{13}C NMR (125 MHz; $CDCl_3$) ***d*** 14.1, 22.6, 23.9, 29.2, 29.2, 30.0, 31.8, 40.4, 55.8, 120.0, 121.5, 126.1, 140.0, 140.5, 151.8; GPC assay in tetrahydrofuran vs. narrow polystyrene standards revealed M_w = 64,600, M_n = 33,000, M_p = 63,100, PDI = 2.0;

Electroluminescent device fabrication

ITO coated glass (a gift from CDT) was cleaned by successive sonication in detergent, 1:1 hydrogen peroxide/ammonia and then distilled water. The PEDOT/PSS (Aldrich, 2.8 wt% solution) was filtered (0.45 µm) and deposited by spin coating at 5000 rpm for 60 sec to give a 75nm layer. The PEDOT/PSS layer was then annealed in an oven at 100 °C for 1 hr. Solutions of the poly(9,9-dioctylfluorene)s in toluene (15 mg/mL) were deposited onto the PEDOT/PSS layer by spin coating. The solutions were filtered (0.2 μm) and then spun at 3000 rpm for 30 sec. The films were annealed at 80 °C for 30 min. Spinning conditions and film thicknesses were optimised for each batch of poly(9,9-dioctylfluorene). In each case the thickness of the poly(9,9-dioctylfluorene) layer was 65±5 nm. All polymer layers were deposited and annealed in air. The cured substrates were transferred to a vacuum evaporator inside a glovebox (H_2O and O_2 levels both < 1 ppm). A layer of LiF (0.2 nm) and then Al (100 nm) were deposited by thermal evaporation at pressures below 2×10^{-6} mbar.

Films were spin coated using a Laurell WS-400B-6NPP Lite single wafer spin processor. A constant acceleration of 10920 rpm was used for all samples. Film thicknesses were determined using a Dektak 6M Profilometer. Electroluminescent devices were tested inside the glovebox (H_2O and O_2 levels both < 1 ppm). Devices were operated using a Kethley 2400 Sourcemeter. The brightness was measured using a Minolta LS-110 Luminance meter. Electroluminescence spectra were recorded using an Ocean Optics USB2000 spectrometer fitted with an optical fibre. The turn-on-voltage was defined as the voltage corresponding to a luminance of 1 cd/m^2. *CIE* coordinates for the devices at their turn on voltage are **8a** (0.21, 0.22), **8b** (0.20, 0.21), **8c** (0.25, 0.36) and **8d** (0.17, 0.15). Subtle shifts in CIE coordinates are probably a consequence of the different end-capping effects.[41]



(a)

(b)

(c)

(d)

Figure S1. Photoluminescence spectra of polymers **8a, 8b, 8c** and **8d** respectively recorded at room temperature in air. Curve (–) pristine; Curve (+) after thermal annealing of the polymers at 110 °C in air for 12 h; Curve (?) after thermal annealing of the polymers at 110 °C in air for 24 h. The characteristic vibronic transition peaks at 438 and 466 nm are indicative of the β-phase.[17,40-42]

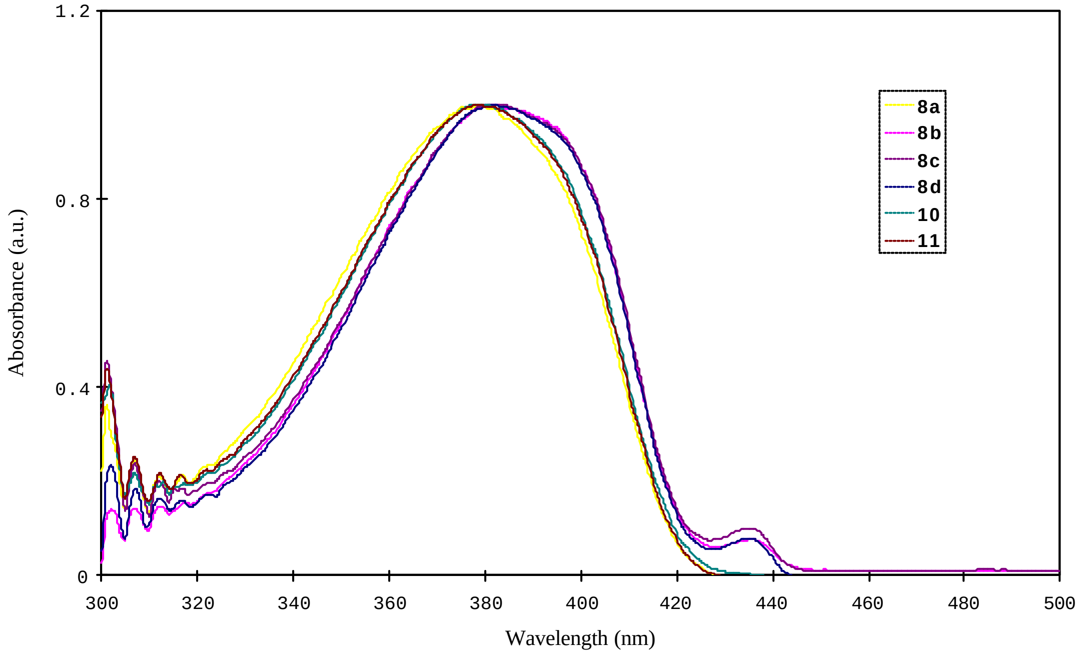


Figure S2. UV-Vis spectra of polymers. **8a-d**, **10** and **11**.

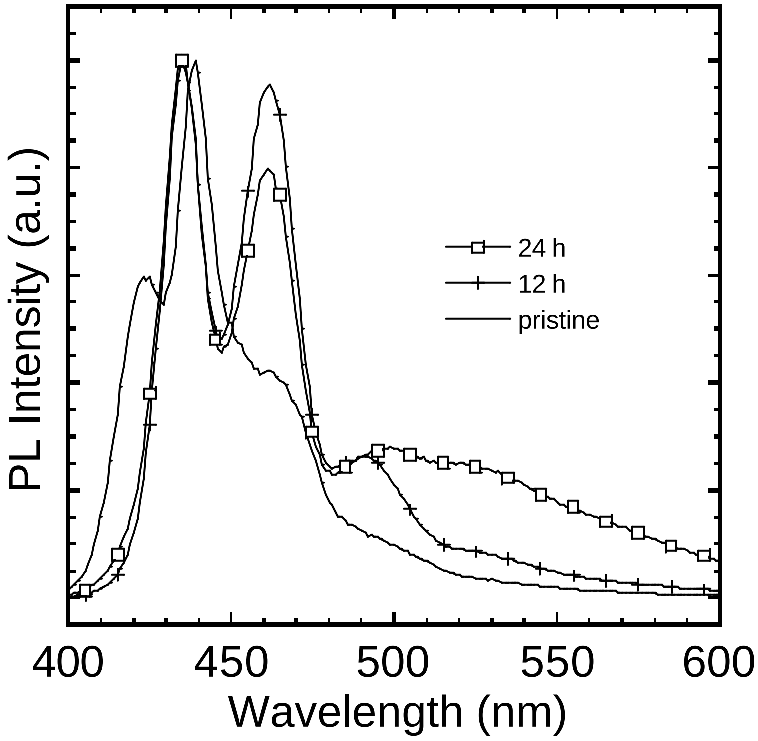


Figure S3. Photoluminescence spectra of polymer **10**, pristine (–), 12 h at 110 °C (+), 24 h at 110 °C (?).

The red shift in the PL spectra of **11** (see Figure 1(b)) compared with **10** is similar to the effect observed by Kulkarni *et al.* who ascribed this to extended conjugation as a result of the increased proportion of fluorenone units.[19]

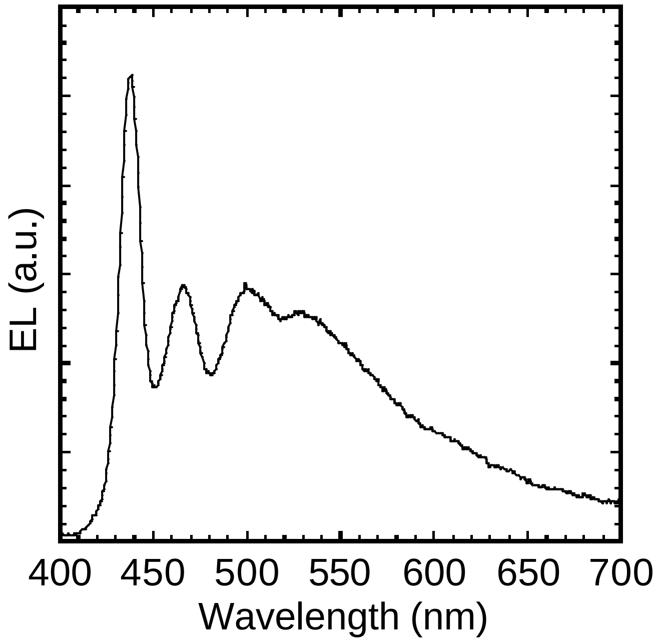


Figure S4. Electroluminescence spectrum of polymer **10** at the turn-on voltage. Device configuration ITO/PEDOT:PSS (70 nm)/Polymer (65 nm)/LiF (0.2 nm)/Al (100 nm).

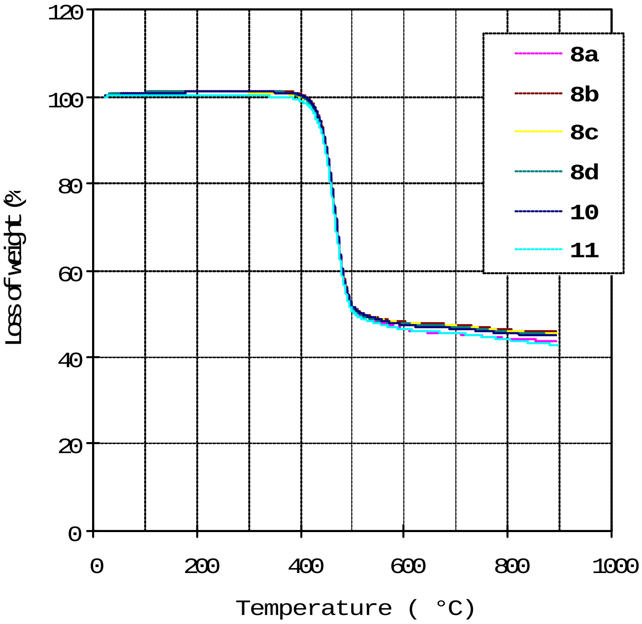


Figure S5. TGA graph of polymers **8a-d**, **10** and **11**.

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