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(54) **Title**: NOVEL BLOCK COPOLYMERS, METHODS OF PREPARATION AND THEIR USE IN HETEROJUNCTION DEVICES

(57) **Abstract**: The invention relates to novel block copolymers having both electron donor and electron acceptor monomer units and to methods for their preparation. A further aspect of the invention relates to the use of the novel block copolymers in the fabrication of polymer film based heterojunction devices. In one form the devices display high conversion efficiencies in solar cell applications.

NOVEL BLOCK COPOLYMERS, METHODS OF PREPARATION AND THEIR USE IN HETEROJUNCTION DEVICES

FIELD OF INVENTION

The present invention relates to novel block copolymers and to methods for their preparation. The invention further relates to the use of the novel block copolymers in the fabrication of polymer film based heterojunction devices. In one form the devices display high conversion efficiencies in solar cell applications.

BACKGROUND

Solid state heterojunctions such as the polymer/organic pn junction between p-type and n-type semiconductors have found widespread application in modern electronics.

Polymer-film based organic photovoltaic (OPV) materials are potentially a competitive alternative to silicon, offering advantages in flexibility, large-scale manufacture by reel-to-reel printing technology, low cost, large area and ease of installation. Polymer devices consist of bulk-heterojunction cells that may be fabricated either using conjugated polymer-fullerene blends or polymer-polymer blends. The standard method of assessing device performance is the efficiency with which solar energy is converted into electrical energy (% ece) which depends on the product of the open circuit voltage (V_{oc}), the short circuit current (J_{sc}) and the fill factor (*FF*) divided by the input power per unit area [see '*Organic Photovoltaics'*, C. Brabec, V. Dyakonov and U. Scherf (Eds.), Wiley-VCH, Weinheim 2008 ISBN: 978-3-527-31675-5; B. A. Gregg *MRS. Bull.* 2005, **30**, 20; B. A. Gregg, *J. Phys. Chem. B*, 2003, **107**, 4688-4698]. Bulk polymer heterojunction solar cells have been fabricated from blends of electron rich donor (Don) homopolymers with electron deficient acceptor (Acc) homopolymers, and it has been disclosed that the efficiency of such devices is improved by the formation of interpenetrating networks of phase-segregated polymers [J. J. M. Halls, C. A. Walsh, N. C. Greenham, E. A. Marseglia, R. H. Friend, S. C. Moratti and A. B. Holmes, *Nature*, 1995, **376**, 498]. The open circuit voltage is determined by the difference in the energy between the Highest Occupied Molecular Orbital (HOMO) of the donor polymer and the Lowest Unoccupied Molecular Orbital (LUMO) of the acceptor polymer.

Solution processible polymers with good film forming ability offer significant advantages over vacuum deposition in the reduction in complexity of steps and the ability to fabricate large area devices.

A possible solution is the formation of a bulk heterojunction device where the two materials are intimately mixed to increase the potentially available interface [G. Yu and A. J. Heeger, *J. Appl. Phys.*, 1995, **78**, 4510-4515]. Upon being mixed, the two materials phase-separate and the final domain size is dependent on the conditions used to form the bulk heterojunction. There is a balance between the generation of a high interfacial area to aid charge separation and the maintenance of a continuous network of paths to the cell electrodes. An idealised structure of a grid of pillars with dimensions of 15nm has been suggested [P. K. Watkins, A. B. Walker and G. L. B. Verschoor, *Nano Lett.*, 2005, **5**, 1814-1818].

Optimum devices fabricated using polymer-polymer blends have realized a % ece of 1.7-1.8 % [C. R. McNeill, A. Abrusci, J. Zaumseil, R. Wilson, M. J. McKiernan, J. J. M. Halls, N. C. Greenham, R. H. Friend, *Appl. Phys. Lett.* 2007, **90**, 193506; C. R. McNeill, J. J. M. Halls, R. Wilson, G. L. Whiting, S. Berkebile, M. G. Ramsey, R. H. Friend, and N. C. Greenham, *Adv. Funct. Mater.*, 2008, **18**, 2309].

There have been a number of attempts to overcome the random structure of the material blends. Block copolymers offer some intrinsic advantages for the control of structure in bulk heterojunctions that appear not to be possible in bilayer or blend devices. Coil-coil block copolymers with electro-active pendant side-chain functionalization have been examined as a potential route to controlling morphology. Controlled morphologies were reported and the block copolymers have improved the device efficiency up to 0.07% [S. M. Lindner, S. Huettner, A. Chiche, M. Thelakkat and G. Krausch, *Angew. Chem. Int. Ed.*, 2006, **45**, 3364-3368; M. Sommer, S. M. Lindner and M. Thelakkat, *Advanced Functional Materials*, 2007, **17**, 1493-1500].

Rod-coil di-block copolymers, where the rod is a conjugated polymer, have been reported significantly to modify morphology in thin films [Y. Nishikitani, T. Asano, S. Uchida, J. Tanimoto: (2003), Photoelectric conversion device, EP 1 482 565 A1; F. Richard, C. Brochon, N. Leclerc, D. Eckhardt, T. Heiser and G. Hadziioannou, *Macromol. Rapid. Commun*, 2008, **29**, 885-891; S. Barrau, T.

Heiser, F. Richard, C. Brochon, C. Ngov, K. van de Wetering, G. Hadziioannou, D. V. Anokhin and D. A. Ivanov, *Macromolecules*, 2008, **41**, 2701-2710; J. Y. Park, N. Koenen, M. Forster, R. Ponnapati, U. Scherf and R. Advincula, *Macromolecules*, 2008, **41**, 6169-6175] although most polymers have not been examined in solar cells.

Rod-rod di- and tri-block copolymers, where the blocks are conjugated, have been examined for their ability to influence morphology in thin films [U. Scherf, A. Gutacker and N. Koenen, *Acc. Chem. Res.*, 2008, **41**, 1086-1097], although few have been examined in photovoltaic cells. It has been reported that inclusion of a flexible non-conjugated linker between the active blocks enables nanoscale structures on the 5-12 nm scale [C. Zhang, S. Choi, J. Haliburton, T. Cleveland, R. Li, S.-S. Sun, A. Ledbetter and C. E. Bonner, *Macromolecules*, 2006, **39**, 4317-4326; S.-S. Sun, *Photovoltaic devices based on a novel block copolymer*, WO 2004/0417185 A1, **2004**, CAN 140:426120; S.-S. Sun, *Sol. Energy Mater. Sol. Cells*, 2003, **79**, 257-264; S. Sun, Z. Fan, Y. Wang, J. Haliburton, C. Taft, S. Maaref, K. Seo and C. E. Bonner, *Synth. Met.*, 2003, **137**, 883-884; S.-S. Sun, *Tandem photovoltaic devices based on a novel block copolymer*, WO 2007/070395 A2, **2007**, CAN 146:484522]. Where devices have been examined the improved device efficiency and improved V_{oc} has been explained by an improved morphology.

Examination of the morphology in thin films formed from all conjugated block copolymers shows a loss of the gross, micron sized features seen in the blends [G. L. Tu, H. B. Li, M. Forster, R. Heiderhoff, L. J. Balk and U. Scherf, *Macromolecules*, 2006, **39**, 4327-4331].

Optical and electrochemical studies of conjugated triblock copolymers have been reported [X. Xiao, Y. Q. Fu, M. H. Sun, L. Li and Z. S. Bo, *J. Polym. Sci. Pol. Chem.*, 2007, **45**, 2410-2424].

It has been recognized that all-conjugated block di- or triblock copolymers may allow self organization into ordered arrays on the nanometer length scale of the order of the exciton diffusion length observed (10 nm) for photovoltaic organic semiconductors. However the only well-defined structures that have been disclosed are amphiphilic conjugated copolymers.

Accordingly, it would be desirable to provide block copolymers that self organize at the nanometer length scale into a suitable morphology for organic

photovoltaic devices. It would be further desirable to provide methods for the preparation of such block copolymers.

SUMMARY OF INVENTION

In a first aspect of the present invention there is provided a block copolymer comprising at least one block of electron donor (D) monomer units and at least one block of electron acceptor (A) monomer units wherein at least one of the blocks has a chain length and polydispersity which are controlled within predetermined ranges. Preferably the block copolymer comprises at least one block that is conjugated. More preferably the block copolymer is fully conjugated. The block copolymer may be a diblock copolymer or a triblock copolymer having a structure ADA, DAD, ADA' or DAD' wherein A and A' represent different electron acceptor blocks and D and D' represent different electron donor blocks. Most preferably the block copolymer is free of amphiphilic substituents.

In one embodiment of the first aspect of the invention the block copolymer comprises a first block of controlled polydispersity and at least one other block formed via a chain extension process performed on the first block.

In a further embodiment of the first aspect of the invention the block copolymer comprises a first block of controlled polydispersity and at least one other block comprising a preformed macromonomeric unit linked to said first block.

In a yet further embodiment of the first aspect of the invention the block copolymer may assemble in the solid phase in length scales of less than or equal to 100 nm, preferably in length scales from between 15 and 40 nm.

Preferably, with respect to any of the aforementioned embodiments, the blocks may be based on repeat units selected from the group consisting of linear, branched, fused or linked aromatic, heteroaromatic, arylene vinylene and heteroarylene vinylene. More preferably, the repeat units comprise a sulphur condensed heterocycle.

In an even yet further embodiment of the first aspect of the invention the energy level of the highest occupied molecular orbital (HOMO) for the electron donor block in the block copolymer is from between -6.5 to -4.5 eV, preferably from between -6.0 to -5.0 eV. Preferably, the energy level of the lowest unoccupied molecular orbital (LUMO) for the electron acceptor block is from

between 1.0 and 2.0 eV higher than the energy level of the highest occupied molecular orbital (HOMO) of the electron donor block, preferably from between 1.0 and 1.6 eV higher than the energy level of the highest occupied molecular orbital (HOMO) of the electron donor block.

In a still yet further embodiment of the first aspect of the invention the energy level of the lowest unoccupied energy level (LUMO) of the electron donor block is at least 0.3 eV higher than the energy level of the lowest unoccupied energy level (LUMO) for the electron acceptor block.

In an even still yet further embodiment of the first aspect of the invention the energy level of the highest occupied molecular orbital (HOMO) for the electron acceptor block is below that of the energy level of the highest occupied molecular orbital (HOMO) for the electron donor block.

In a preferred form of the first aspect of the present invention the polydispersity of one of the blocks of the block copolymer is less than or equal 2.0. More preferably the polydispersity of one of the blocks is less than or equal 1.5.

In a further preferred form of the first aspect of the invention the chain length of at least one of the blocks of the block copolymer is such that the number average molar mass is between 4,000 and 100,000 Daltons.

In a second aspect of the present invention there is provided, in one embodiment, a method of preparing a conjugated block copolymer comprising providing a first block of controlled polydispersity and chain extending the said first block.

In a further embodiment of the second aspect of the present invention there is provided a method of preparing a conjugated block copolymer comprising providing a first block of controlled polydispersity and coupling to at least one end of said first block a preformed macromonomeric unit.

Preferably the polydispersity of the first block may be controlled through polymerisation, for example by controlled living or quasi living polymerisation, quasi living Suzuki polycondensation or living free radical polymerisation for non-conjugated polymers.

Alternatively or additionally the polydispersity may be controlled through physical separation, for example by solubility difference or chromatography.

The present invention provides methods for the controlled synthesis of block copolymers that do not contain amphiphilic substituents, and their surprising ability to self organize at the nanometer length scale into a suitable morphology for organic photovoltaic devices. A surprising improvement in photovoltaic device efficiencies is observed over devices fabricated using blends of the corresponding homopolymers fabricated from the individual monomeric components.

Employing conjugated ADA triblock copolymers based on triarylamine, 9,9-dioctylfluorene and benzothiadiazole comonomers reveals a surprising ability to control the morphology of the triblock copolymer on the nanoscale. A general feature of the invention is to control the polydispersity of the central 'D' block and to chain extend this block at both ends with the 'A' blocks. The 'D' block may be endcapped with an easily functionalized site, and by virtue of this unsubstituted terminus, can be further chain-extended with conjugated substituents such as triaryl amines, aryl and heteroaryl groups using a variety of methods such as Suzuki, Stille, Buchwald-Hartwig, Sonogashira, Ulmann and Heck cross coupling or with non-conjugated blocks by any of the recognized living free radical methods, such as RAFT, ATRP or nitroxide mediated living polymerisation. Alternatively the 'D' block may be coupled at each end using macromonomeric 'A' block units. The 'D' block may be selected from any polymer based on a conjugated comonomer building block. The A and D blocks may be selected from, but not limited to, monomers based on linear, branched, fused or linked aromatic, heteroaromatic, arylene vinylene, heteroarylene vinylene repeat units. Exemplary aromatic units may be phenylene, fluorenyl, naphthyl, perylene, coronene, rylene, and other condensed aromatic structures. Illustrative heteroaromatic structures embedded conjugatively in the main chain include thienyl, pyridyl, benzothiadazolyl, quinoline, oxadiazolyl, pyrazine, triazine, quinoxaline, porphyrine, phthalocyanine and their vinylene or ethynyl chain extended derivatives. These conjugated units can be incorporated either linearly or as a dendron. Blocks for living free radical polymerisation may be selected from vinyl monomers carrying donor (Don) or acceptor (Acc) pendant groups, for example, styrenic, acrylic, methacrylic, acrylamide or methacrylamide monomers carrying Acc or Don substituents. Preferred examples have UV/VIS absorption corresponding with the solar spectrum. A most preferred illustrative example consists of the triaryl-amine based repeat unit for the 'A' block known as 'PFM' **1**

and the fluorenyl benzothidiazole based repeat unit known as 'F8BT' for the D block. Polymers incorporating these design principles but with optimised capacity to absorb AM1.5 solar spectrum are preferred.

Furthermore, the functionalised endcap of the 'D' block may itself be a reactive group or may be readily converted into a functional group and may consist of, for example an aryl halide, trimethylsilyl-aryl, nitro-aryl, an acid labile diacetal or tert-butyl ester or other groups known in the literature, which generate a functional group on reaction.

The 'D' block may be derived from a selection of repeat units in combination having a number average molar mass range of 4,000-100,000, most preferably 4,000-30,000 and having an extended length 10-30 nm. The 'A' block may be derived from a selection of the above repeat units singularly or in combination. In order to realize the preferred morphology of a ADA triblock copolymer with domains of preferred length scale 15-20 nm extending through the active layer to the relevant charge-collecting electrode, the length of each 'A' block should range from being preferably on average equal to the length of the 'D' block to most preferably on average being in the range of half the length of the 'D' block.

The invention also provides AD block copolymers having similar features to those described above.

For an AD block copolymer the preferred range of the 'A' block will fall in the length scale range of being between equal to twice the length of the 'D' block.

The invention also provides ADA block copolymers in which the 'D' block consists of a styrenic, acrylic or methacrylic homopolymer carrying pendant conjugated side chains from a selection of the repeat units described above and constructed by controlled free radical polymerization. The D' block may be chain extended or connected with 'A' block polymers as described above.

Another feature of the present invention is the selection of a suitable conjugated rigid rod 'D' block which is chain extended by living polymerization using styrenic, acrylic or methacrylic monomers carrying pendant conjugated side chains from a selection of the repeat units described above.

Morphology may be developed in any of a number of known methods including thermal annealing, solvent annealing or the use of an additive which modifies the thin film morphology but does not remain in the film [N. E. Coates,

I.-W. Hwang, J. Peet, G. C. Bazan, D. Moses and A. J. Heeger, *Appl. Phys. Lett.*, 2008, **93**, 072105/072101-072105/072103]. The thin film morphology may be modified by using these techniques singularly or in combination.

In a third aspect of the present invention there is provided a heterojunction device comprising as an active component one or more of the copolymers hereinbefore disclosed. The heterojunction device may further comprise one or more electron donors or electron acceptors.

In a fourth aspect of the present invention there is provided a photovoltaic cell comprising a heterojunction device as hereinbefore disclosed.

In a fifth aspect of the invention there is provided a use of a heterojunction device as hereinbefore disclosed in the generation of solar power. Solar cells may be fabricated on a large scale and high solar energy efficiencies may be obtained.

Throughout this specification, use of the terms 'comprises' or 'comprising' or grammatical variations thereon shall be taken to specify the presence of stated features, integers, steps or components but does not preclude the presence or addition of one or more other features, integers, steps, components or groups thereof not specifically mentioned.

BRIEF DESCRIPTION OF THE FIGURES

Figure 1 shows AFM micrograph images of PFM|F8BT homopolymer blend and PFM-F8BT-PFM triblock copolymer films. Figures (a) and (b) show PFM|F8BT homopolymer blend films with micron size domains. No nanoscale features are obvious in the 1x1 mm micrograph (b). Images (c)-(f) are of the PFM-F8BT-PFM block copolymer films, (c) and (d) unannealed, (e) and (f) annealed at 140°C for 1 hour, (g height) & (h phase) annealed at 140°C for 3 hours.

Figure 2 shows the spectroscopic analysis of Polymer A (PFM-F8BT-PFM block co-polymer) compared directly to a 1:1 blend of the homo-polymers, PFM:F8BT. The UV-Vis absorbance is recorded on the left hand axis while the fluorescence emission is recorded on the right hand axis. The excitation wavelength was 350 nm, where both the components have significant absorption. The numbers are absolute.

Figure 3 shows the GPC of chain extended Block B1 central core to form Polymer A, the triblock copolymer PFM-F8BT-PFM. The final polymer

eight ratio of PFM to F8BT is 1:1, increasing from Block B1 (M_n = 21,200, M_w = ?,000 , M_w/M_n = 1.50) to Polymer A (M_n = 43,500, M_w = 56,400, M_w/M_n = 1.30).

Figure 4 shows the GPC trace for Block B1 generated by removing all the w molecular weight, ethyl acetate soluble, material from the precursor material.

ETAILED DESCRIPTION OF THE INVENTION

It will now be convenient to describe the invention with reference to articular embodiments and examples. These embodiments and examples are ustrative only and should not be construed as limiting upon the scope of the vention. It will be understood that variations upon the described invention as

would be apparent to the skilled addressee are within the scope of the invention. Similarly, the present invention is capable of finding application in areas that are not explicitly recited in this document and the fact that some applications are not specifically described should not be considered as a limitation on the overall applicability of the invention.

Illustrative examples of the synthesis and device characterization of two triblock conjugated polymers are set out below.

It is possible to employ a number of techniques to modify the polydispersity (PDI) of a polymer and a central polymer block with a well-defined molecular weight and narrow PDI is important to drive controlled phase separation. The size on the central 'D' block may be controlled by use of controlled living or 'quasi' living polymerization techniques such as GRIM [R. S. Loewe, P. C. Ewbank, J. Liu, L. Zhai and R. D. McCullough, *Macromolecules*, 2001, **34**, 4324-4333], 'quasi' living Suzuki polycondensations, living free radical polymerizations (Raft, ATRP, Nitroxide mediated, reverse ATRP etc), macromonomer synthesis solubility difference, or chromatographic techniques including size exclusion chromatography or column chromatography.

An endcap functionalised F8BT polymer was synthesized by standard Suzuki condensation polymerization methods to generate a polymer with a number average molecular weight of 10,000-20,000. This method generates a central 'D' block with a PDI of >1.5. The central 'D' block size was then controlled by the selective removal of all short chain fractions based on relative solubility in selected solvents resulting in a central 'D' block with a PDI of <1.5. The removal of short chain oligomers or polymers may be effected by solubility difference through recrystallisation or continuous extraction processes. The short chain F8BT oligomers / polymers of central 'D' block were removed by Soxhlet extraction with selected solvents. It is possible to control the removal of fractions by solvent choice. Evidence of block copolymer formation is delivered by standard analysis by GPC where block copolymer formation is indicated by an increase in the average number average and peak molecular masses.

Fluorescence quenching

It is known in the art that fluorescence quenching in the blend is an important first indicator to device performance and indicates energy and/or

electron transfer from the Donor to the Acceptor or the Acceptor to the Donor. It is an important but not essential indicator. It would be expected in a block copolymer that fluorescence quenching, with a well ordered structure and physically linked blocks, would be enhanced. A further indication that energy transfer and charge separation has occurred is the generation of an exciplex emission. The exciplex is an interface bound hole electron pair which may decay via emission leading to a fluorescence emission peak which is at a longer wavelength than for either of the two component polymers and has a longer lifetime [J. Cabanillas-Gonzalez, T. Virgili, G. Lanzani, S. Yeates, M. Ariu, J. Nelson and D. D. C. Bradley, *Phys. Rev. B*, 2005, **71**, 014211/1-8]. Exciplex formation is considered to be one of the three steps in photocurrent generation, a) electron transfer, b) exciplex formation and c) transfer of the charge to the collecting electrode.

Morphology

Thin film formation with homopolymer blends is characterized by large and small-scale features, with the large-scale features on the micron scale with small scale features on the nanometer scale. The scale of the feature sizes is variable and is dependent on method of film formation, solvent pre-and post film formation treatment, for example extended thermal annealing in homopolymer blends leads to greater phase segregation with loss of device performance. A feature of thin film morphology should be that the morphology is less dependent on the deposition condition and pre and post film formation treatments. It is known that extended annealing of non-conjugated block copolymers leads to well-defined nanostructure with feature lengths dependent on block size. Atomic Force Microscopy (AFM) is used as the primary technique to examine morphology in thin films.

Improved morphological features for thin films formed from block copolymers should result in more of the material being within diffusion distance of photogenerated excitons and formation of extended interpenetrating networks leading to the collecting electrodes and therefore lead to improved device efficiencies.

EXAMPLES

Example 1

Devices

Devices formed from triblock copolymers formed from F8BT and PFM

Standard device configures were used to assemble devices using homopolymer blends of F8BT and PFM along with a triblock copolymer. The devices had the following architecture, ITO|PEDOT:PSS (60 nm)|active layer|Ca (20 nm)|Al (100nm), and were assembled in a glove box under a nitrogen atmosphere. The thickness of the active layer is as indicated in Table 2 below. The cells were tested with an Oriel solar simulator fitted with a 1000W Xe lamp filtered to give an output of 100mW/cm^2 at AM 1.5. The lamp was calibrated using a standard, filtered Si cell from Peccell Limited. Prior to analysis the output of the lamp was adjusted to give a J_{SC} of 0.605 mA with the standard device. The devices were tested using a Keithley 2400 Sourcemeter controlled by Labview Software.

Device data is recorded in Table 2 and comparing device efficiency for CI2 (triblock copolymer, Polymer A) compared to CI1 (homopolymer blend) indicates an improved performance for Polymer A (triblock copolymer) for devices with an active layer of 50 or 100nm.

Table 1: Details of device active layer formulation with PFM:F8BT homopolymer blends or a PFM-F8BT-PFM triblock copolymer (Polymer A)

Sample					spin speed	average t
Device	PFM (mg)	F8BT (mg)	Polymer A (mg)	Blend details	rpm	nm
CI1	10	10	0	0.5mL(10mg/0.5mL) PFM+ 0.5mL(10mg/0.5mL) F8BT in CB*	8000	65
CI2	0	0	10	0.67mL(10mg/0.67mL) DJJ210 in CB	3000	50
CI3	10	10	0.8	0.5mL(10mg/0.5mL) PFM+ 0.5mL(10mg/0.5mL) F8BT in CB	3000	100
CI4	0	0	10	0.67mL(10mg/0.67mL) DJJ210 in CB	800	100

* chlorobenzene

Table 2: Solar Cell Device data for active devices containing PFM:F8BT homopolymer blends or PFM-F8BT-PFM triblock copolymers

Device	Pixel	Area input	Actual Area (cm2)	Light power (W/cm2)	Voc (V)	Isc (A)	Isc (A/cm2)	FF	Pmax (W/cm2)	V at Pmax	Power Efficiency
1	1	0.2	0.2	0.1	1.35	5.43E-05	2.71E-04	0.22	1.64E-05	6.60E-01	0.02
1	2	0.2	0.2	0.1	1.40	5.49E-05	2.75E-04	0.22	1.68E-05	6.70E-01	0.02
1	3	0.2	0.2	0.1	0.18	5.72E-05	2.86E-04	0.29	2.96E-06	1.00E-01	0.00
1	4	0.2	0.2	0.1	1.41	5.88E-05	2.94E-04	0.22	1.80E-05	6.40E-01	0.02
2	1	0.2	0.2	0.1	1.02	2.96E-04	1.48E-03	0.26	7.82E-05	5.20E-01	0.08
2	2	0.2	0.2	0.1	1.28	3.05E-04	1.52E-03	0.23	8.83E-05	5.80E-01	0.09
2	3	0.2	0.2	0.1	1.00	6.02E-04	3.01E-03	0.23	1.40E-04	4.60E-01	0.14
2	4	0.2	0.2	0.1	1.34	2.99E-04	1.50E-03	0.23	9.02E-05	6.50E-01	0.09
3	2	0.2	0.2	0.1	1.46	1.79E-05	8.96E-05	0.21	5.42E-06	6.50E-01	0.01
3	3	0.2	0.2	0.1	1.42	1.74E-05	8.68E-05	0.21	5.17E-06	6.50E-01	0.01
3	4	0.2	0.2	0.1	0.35	4.45E-05	2.23E-04	0.30	4.66E-06	1.90E-01	0.00
4	1	0.2	0.2	0.1	1.41	9.14E-05	4.57E-04	0.22	2.80E-05	6.60E-01	0.03
4	2	0.2	0.2	0.1	0.97	1.11E-04	5.54E-04	0.25	2.72E-05	4.60E-01	0.03
4	3	0.2	0.2	0.1	1.30	1.03E-04	5.14E-04	0.23	3.12E-05	6.60E-01	0.03
4	4	0.2	0.2	0.1	1.35	7.73E-05	3.87E-04	0.23	2.35E-05	6.50E-01	0.02

Example 2

Morphology

Thin films were deposited from toluene solution on to glass substrates and examined by Atomic Force Microscopy (AFM), 20mg/ml solution spin coated at 2000 rpm onto glass substrates. Indicative results are shown in Figure 1. Figure 1a and 1b show AFM micrographs (5 x 5 micron and 1 x 1 microns) height profiles for typical films formed from homopolymer blends of PFM and F8BT. The vertical height varies by up to 30 nm while the lateral feature sizes are of the order of 0.5 to 1.0 microns. There is no obvious fine structure on the nanometer scale evident. Figures 1c and 1d show typical height profiles for thin films formed by spin coating Polymer A (PFM-F8BT-PFM triblock copolymer) onto a glass substrate. Micrograph lengthscales are now 1.0 micron and 0.25 micron

respectively with a recorded vertical variation in height of only 3-10 nm indicated. Fine structure with lateral features of the order of 20-30 nm are evident.

Annealing the films at 140°C for 60 minutes did not lead to any significant change for the homopolymer blend but resulted in well defined lateral structures of the order of 15-30 nm for Polymer A, Figures 1e and 1f.

Extended annealing of Block copolymer films, 140°C for 3 hours, leads to improved phase development, Figure 1g (height) and 1h (phase image).

Example 3

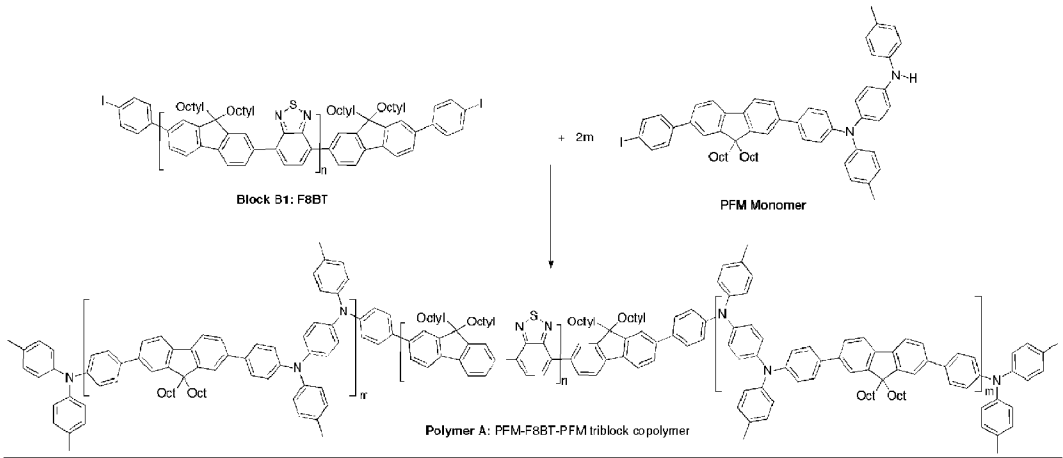
Spectroscopy

UV-Vis absorbance spectra and fluorescence spectra for the homopolymer blends and Polymer A are recorded in Figure 2. The PFM:F8BT homopolymer blend and the PFM-F8BT-PFM triblock copolymer show effectively identical absorption spectra. The fluorescence emission spectra show significant variation between the active materials. Fluorescence emission from the PFM:F8BT homopolymer blend is from both the PFM (450 nm) and F8BT (540 nm) homopolymers. In the block copolymer, the fluorescence emission is completely quenched from the PFM part of Polymer A while the emission is significantly quenched from the F8BT block in Polymer A. The flat extended region of the emission spectrum from the Polymer A (PFM-F8BT-PFM triblock copolymer) has been identified as emission (620 nm) from an exciplex with an extended lifetime of 31.5 ns.

Example 4

Synthesis of Polymer A (PFM-F8BT-PFM, triblock copolymer)

Scheme 1: Synthesis of Polymer A (PFM-F8BT-PFM triblock copolymer) by chain extension of a narrow PDI central F8BT core (Block 'B')



A 100ml RB flask was charged with **IC_6H_4–(F8BT)$_n$F8–C_6H_4I** (**Block B1**, n=25, 0.592 g, 0.04 mmole), **PFM monomer** (0.684 g, 0.716 mmole) and $Pd(OAc)_2$ (9.0 mg, 0.04 mmole) and the flask pumped into a glovebox. The flask was then charged with Na^{t}OBu (0.21 g, 2.1 mmole) and fitted with a suba seal before being removed from the glovebox. Dry, degassed toluene (20 ml) was added under nitrogen then ^{t}Bu$_3$PH[BF_4] (11.6 mg, 0.04 mmole). The reaction mix was heated to 80ºC for 16 hours. Di-tolylamine (0.2 g, excess) was added and the reaction stirred at 80ºC for an extra 6 hours. The reaction mix was cooled to ambient and the aqueous phase decanted and the organic phase washed with 2 x 5mls of H_2O. The organic phase was filtered through a plug of silica and the solvent volume reduced to ~5 ml. The product was precipitated by dropwise addition to 250 ml of rapidly stirred methanol, collected by filtration, washed with methanol and dried in air (1.10 g, 93%).

^{1}H-NMR (500MHz, C_6D_6): δ_H 8.470(s, 4H, Ar-H), 8.126(brm, 2H, Ar-H), 7.974(brd, 2H *J* = 7.5 HZ, AR-H), 7.76-7.65(M, 5.2H, AR-H), 7.582(brd, 4.9H *J* = 8.7 Hz, Ar-H), 7.300(brd, 3H *J* 8.5 Hz, Ar-H), 7.22-7.12(m, *overlapping solvent*, Ar-H), 6.963(brd, 3.3H *J* = 8.5 Hz, Ar-H), 2.40(brs, 3H, F8BT-α-CH_2), 2.14(brm, 8H, PFM-α-CH_2& Ar-Me's), 1.33-0.95(m, 48H, CH2's), 0.78(m, 12H, alkyl-Me's),

0.495(brs, 3H, alkyl-CH_2's).^{13}C NMR (125 MHz, C_6D_6): ^{13}C-NMR (100 MHz, C_6D_6): δ_C154.9, 152.1, 147.9, 145.8, 143.5, 141.5, 140.43, 140.35, 137.3, 135.7, 133.9, 132.9, 130.4, 129.0, 126.3, 125.7, 125.2, 124.9, 14.8, 124.7, 123.7, 121.3, 120.6, 6.1, 55.7, 41.1, 32.2, 32.1, 30.7, 30.5, 29.7, 29.6, 29.5, 29.0, 24.7, 24.4, 23.0, 20.8, 14.3. Elemental analysis: Calculated for $(PFM)_{20}(F8BT)_{25}$ = $C_{2095}H_{2370}N_{90}S_{25}$ C, 84.97; H, 8.07; N, 4.26; S, 2.71. Found C, 82.49; H, 8.42; N, 1.84; S, 2.56. GPC: M_n, 43500; M_w, 56354; M_p, 49022; M_w/M_n, 1.29.

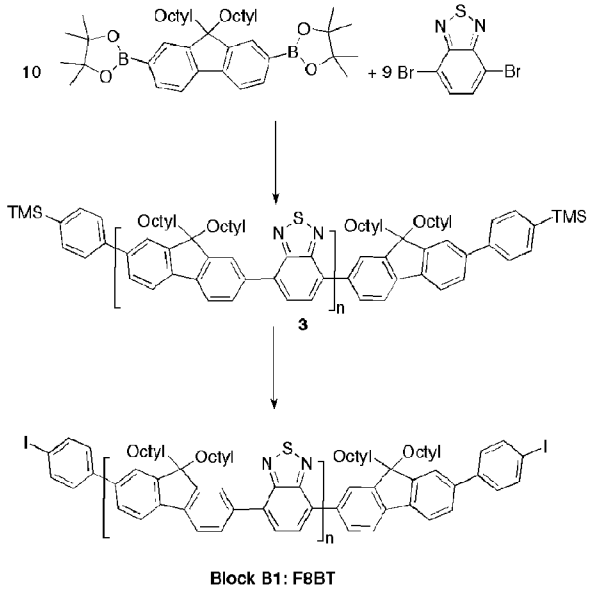
The formation of a triblock PFM-F8BT-PFM copolymer, Polymer A, is indicated by the chain extension, see GPC trace Figure 3.

Example 5

Synthesis of F8BT central core Precursor

Block B Precursor: 7,7'-bis(4-iodophenyl)-poly-(9,9-dioctyl-9H-fluoren-2-ene)-alt-4,4'-benzo[c][1,2,5]thiadiazole

Scheme 2: Synthesis of central sized Block B1 (F8BT) via a Suzuki poly-condensation reaction followed by Soxhlet extraction



To compound **3** (n = 40) (3.86 g, 0.65 mmole) dissolved in 500 ml of dry, degassed DCM at 0°C was slowly added ICl (1M, 1.5 ml, 1.5 mmole) until the colour persisted. The excess ICl was deactivated by addition of saturated sodium

thiosulphate solution until the colour of ICl was discharged. The organic phase was washed with water and dried over $MgSO_4$. The solvent was reduced under vacuum to ~20 ml and the product precipitated by adding the DCM solution dropwise to 500 ml of rapidly stirring methanol. The product was collected by filtration, washed with methanol and dried under a stream of air, then overnight under high vacuum (3.90 g, 99%).

^{1}H-NMR (500MHz, C_6D_6): δ_H 8.497(brs, 2H, Ar-H), 8.420*(s, 0.23H, Ar-H), 8.138(brs, 2H, Ar-H), 8.089*(brd, 0.29H J = 8.5 Hz, Ar-H), 7.961(m, 2H, Ar-H), 7.880*(brd, 0.3H J = 7.8 Hz, Ar-H), 7.73-7.57(brm, 2.6H, Ar-H), 7.608*(brd, 0.50H J = 7.8 Hz, Ar-H), 7.435*(brd, 0.2H, Ar-H), 7.176(d, *overlapping solvent*, Ar-H), 2.39-2.17(brm, 4H, octyl-α-CH2's), 1.3-1.1(brm, 29H, octyl-CH_2's), 0.806(brt, 7.4H, octyl-Me's). *end-groups and F8 near chain end.^{13}C NMR (125 MHz, C_6D_6): δ_C154.9, 152.1, 141.6, 138.2, 137.3, 133.9, 129.4, 129.0, 124.8, 120.6, 56.1, 55.9w, 41.1, 41.0w, 32.2, 30.7, 30.6w, 29.7, 29.6w, 24.7, 24.5w, 23.0, 14.3. Elemental analysis: Calculated for $IC_6H_4(F8BT)_nF8C_6H_4I$ (n = 40), $C_{1447}H_{1746}N_{80}S_{40}I_2$, C, 79.74; H, 8.07; N, 5.14; S, 5.88. Found C, 77.67; H, 8.17; N, 4.62. GPC (UV-Vis, λ = 325, toluene): M_n, 6,500; M_w, 16,800; M_p, 20,000; M_w/M_n, 2.59.

Example 6

Block B1: F8BT central core.

7,7'-bis(4-iodophenyl)-poly-(9,9-dioctyl-9H-fluoren-2-ene)-alt-4,4'-benzo[c][1,2,5] thiadiazole

The polymer central Block B precursor (n = 32, 3.6 g) was placed in a Soxhlet extractor and extracted with refluxing ethyl acetate for 24 hours. The insoluble fraction was recovered and dried in a stream of air and then under high vacuum to generate **Block B1**: EtOAc insoluble (2.67 g, 74.2%).

^{1}H-NMR (500MHz, C_6D_6): δ_H 8.496(brs, 2H, Ar-H), 8.420*(s, 0.15H, Ar-H), 8.142(brs, 2H, Ar-H), 8.095*(brd, 0.15H, Ar-H), 7.972(m, 2H, Ar-H), 7.884*(brd, 0.15H, Ar-H), 7.73-7.57(brm, 2.4H, Ar-H), 7.608*(d, 0.30H J = 8.2 Hz, Ar-H), 7.435*(brd, 0.15H, Ar-H), 7.153(d, *overlapping solvent*, Ar-H), 2.39-2.17(brm, 4H, octyl-α-CH_2's), 1.3-1.1(brm, 29H, octyl-CH_2's), 0.806(brt, 7.2H, octyl-Me's). *end-groups and F8 near chain end. ^{13}C NMR (125 MHz, C_6D_6): δ_C154.9, 152.1, 141.6,

138.2, 137.3, 133.9, 129.4, 129.0, 124.8, 120.6, 56.1, 55.9w, 41.1, 41.0w, 32.2, 30.7, 30.6w, 29.7, 29.6w, 24.7, 24.5w, 23.0, 14.3

Batch 1: Elemental analysis: Calculated for $IC_6H_4(F8BT)_nF8C_6H_4I$ (n = 40), $C_{1447}H_{1746}N_{80}S_{40}I_2$, C, 79.74; H, 8.07; N, 5.14; S, 5.88. Found C, 77.68; H, 8.17; N, 4.62. GPC (UV-Vis, λ = 325, toluene): M_n, 14,000; M_w, 21,000; Mp, 21,000; M_w/M_n, 1.50.

Example 7

Block B2: F8BT central core

As above for Block B1 using ethyl propionate as the extracting solvent. GPC (UV-Vis, λ = 325, toluene): M_n = 24,600, M_w = 34,400, M_w/M_n = 1.40.

Example 8

Compound 3: 7,7'-bis(4-trimethylsilylphenyl)-*poly*-(9,9-dioctyl-9*H*-fluoren-2-ene)-*alt*-4,4'-benzo[*c*][1,2,5]thiadiazole

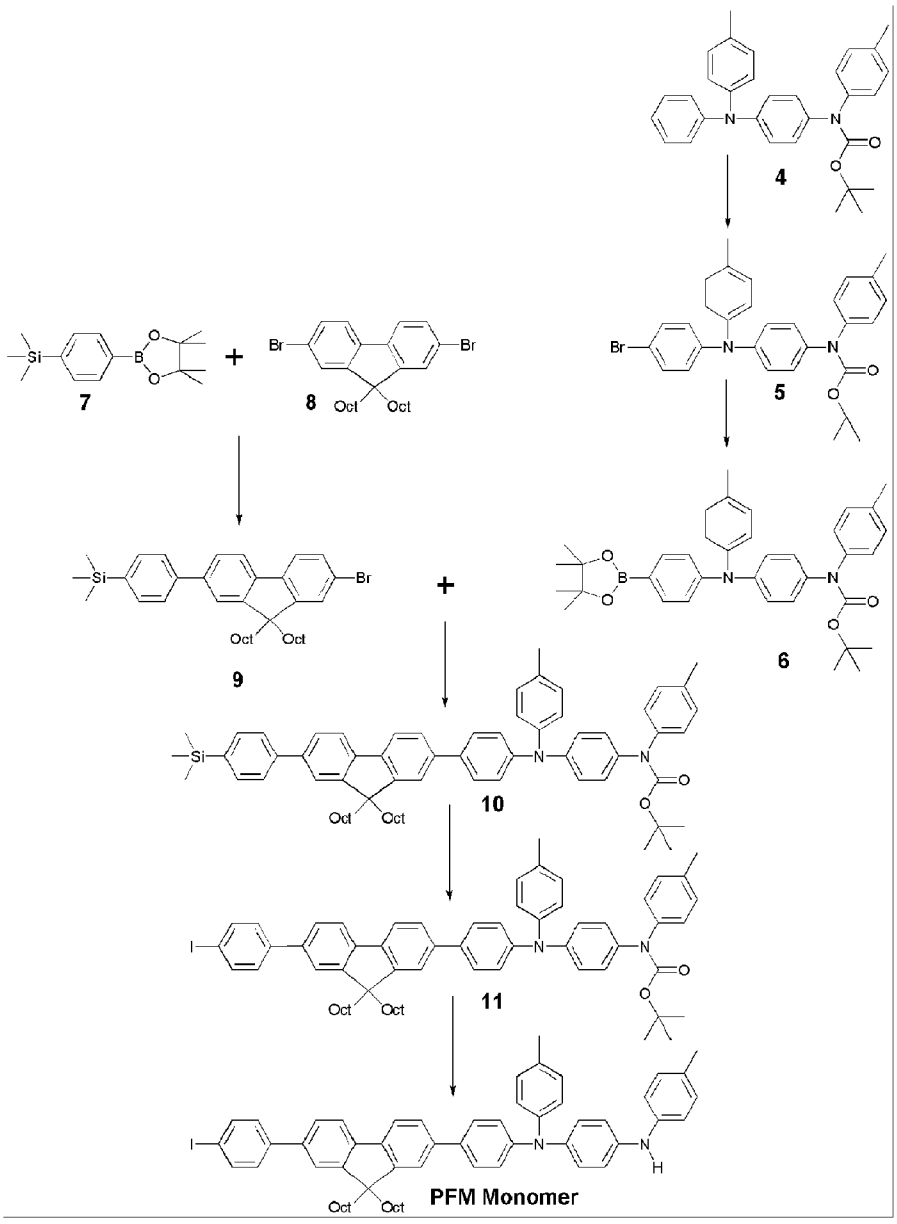
A 250ml RB flask was loaded with 2,2'-(9,9-dioctyl-9*H*-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (5.0 g, 7.789 mmole) and 4,7-dibromobenzo[*c*][1,2,5]thiadiazole (2.08 g, 7.07 mmole) then toluene (100 ml) and Et_4NOH (20 Wt%, 40 ml) and the biphasic reaction mix degassed by bubbling nitrogen through for 30 minutes. The catalyst, $Pd(PPh_3)_4$ (0.162 g, 0.14 mmole), was added and nitrogen bubbling continued for 10 minutes. The reaction mix was heated to 80°C for 16 hours then (4-bromophenyl)trimethylsilane (0.5 g, excess) added and the reaction continued for 6 hours. The reaction mix was cooled and the aqueous phase decanted and the organic fraction washed with 2 x 20 ml of water then filtered through a pad of silica. The solvent volume was reduced to ~30 ml and the product precipitated by dropwise addition of the toluene solution to 500 ml of rapidly stirred methanol. The product was recovered by filtration, washed with methanol and dried under a stream of air (4.12 g, 98.5%).

^{1}H-NMR (500MHz, C_6D_6): δ_H 8.477(brs, 2H, Ar-H), 8.113(brs, 2H, Ar-H), 7.95-7.86(m, 2.13H, Ar-H), 7.77-7.58(m, 3.8H, Ar-H), 2.39(brm, 4H, octyl-α-CH_2), 1.30-1.10(m, 29.31H, octyl-CH_2's), 0.782(m, 7.2H, octyl-Me's), 0.272(s, 2.0H, SiMe's). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C154.4, 152.0*, 171.8, 151.5*, 142.1*, 141.0*, 140.9, 140.3*, 139.2*, 136.2, 136.2*, 133.9, 133.63, 133.55*, 128.3,

128.0, 126.6, 126.5*, 126.1*, 124.0, 123.9*, 121.7, 120.2*, 120.1, 119.8*, 55.5, 55.4*, 40.2, 31.8, 30.14, 30.07, 29.3, 24.1, 23.9, 22.6, 14.1, -1.1. * low intensity peaks.

Batch 1: Elemental analysis: Calculated for TMS-C_6H_4(F8BT)$_n$F8C_6H_4-TMS (n = 40), $C_{1447}H_{1746}N_{80}S_{40}Si_2$, C, 80.4; H, 8.15; N, 5.19; S, 5.94. Found C, 80.6; H, 8.58; N, 4.65; S, 4.74.GPC (UV-Vis, λ= 325, toluene): M_n 7,900; M_w 24,600; M_p 32,100; M_w/M_n 3.10.

Scheme 3: Synthetic pathway to AB functionalised PFM monomer for chain extension of Block B1



Example 9

PFM Monomer: *N*1-(4-(7-(4-iodophenyl)-9,9-dioctyl-9*H*-fluoren-2-yl)phenyl)-*N*1,*N*4-di*p*-tolylbenzene-1,4-diamine

To a solution of **11** (3.0g, 2.85 mmole) in DCM (100mls) under nitrogen at 0ºC was added trifluoroacetic acid (5.0 ml, excess) and the reaction mix stirred for 2 hours while warming to ambient. An excess of Et_3N was added and the solvent removed under vacuum. The residue was slurried in toluene and filtered through a pad of silica. The toluene was removed under vacuum to leave a yellow reside. The residue was dissolved in a minimum of ether (3-5 ml) and the product precipitated by adding the ether solution dropwise to 250 ml of rapidly stirred methanol at -15ºC. The pale yellow product was recovered by filtration, washed with cold methanol and dried in a stream of air and then under vacuum overnight (2.071 g, 76%).

^{1}H-NMR (500MHz, C_6D_6): δ_H 7.752(d, 1H J = 1.3 Hz, Ar-H), 7.658(d, 1H J = 7.9 Hz, Ar-H), 7.636(d, 1H J = 7. Hz, Ar-H), 7.59-7.54(m, 6H, Ar-H), 7.360(dd, 1H J = 7.9 & 1.7 Hz, Ar-H), 7.268(d, 2H J = 8.7 Hz, Ar-H), 7.180(d, 2H J = 8.4 Hz, Ar-H), 7.13-7.08(m, 4H, Ar-H overlapping solvent), 6.937(dd, 4H J = 8.1 & 5.9 Hz, Ar-H), 6.838(d, 2H J = 8.4 Hz, Ar-H), 6.775(d, 2H J = 8.8 Hz, Ar-H), 4.91(s, 1H, N-H), 2.118(s, 3H, Me) and 2.106(s, 3H, Me) overlapping (bm, 4H, octyl-α-CH_2s), 1.13-0.90(bm, 24H, octyl-CH_2's), 0.767(t, 6H, J = 7.2 Hz, octyl-Me's). ^{13}C NMR (125 MHz, C_6D_6): δ_C 152.25, 152.13, 148.42, 146.05, 141.51, 141.32, 141.18, 141.08, 140.98, 140.42, 139.81, 139.40, 138.18, 134.81, 132.33, 130.48, 130.28, 130.13, 129.38, 127.04, 126.52, 126.30, 124.61, 122.87, 121.46, 121.32, 120.72, 120.51, 118.77, 118.67, 93.06, 55.74, 46.77, 40.93, 32.10, 30.47, 29.58, 29.49, 24.35, 22.94, 20.81, 20.73, 14.28. m.p.: 77-78°C(dec). EI *m/z* 955(M+, 100%). Elemental Analysis: Calculated for $C_{61}H_{67}IN_2$ C, 76.71; H, 7.07; I, 13.29; N, 2.93. Found C, 76.65; H, 7.06; N, 3.10.

Example 10

Compound 11: *tert*-butyl 4-((4-(7-(4-iodophenyl)-9,9-dioctyl-9*H*-fluoren-2-yl)phenyl)(*p*-tolyl)amino)phenyl(*p*-tolyl)carbamate

To a solution of **10** (4.163 g, 4.16 mmole) dissolved in dry degassed DCM (150 ml) at -20°C was added ICl (14.6 ml, 1.0M in DCM, 14.6 mmoles) dropwise

over 20 minutes. The solution went a dark green. The reaction mix was stirred at -20°C for 3 hours then and excess of Et_3N (5 ml) added. The reaction mix was deactivated by addition of an excess of saturated sodium thiosulphate solution. The organic phase was separated and the reaction mix extracted with DCM (2 x 50 ml). The combined organic phase was washed with brine and dried over $MgSO_4$. The solvent was removed under vacuum. The product was purified by column chromatography, toluene R_f = 0.43, then by dissolving in a minimum of ether and adding the ether solution dropwise to 250 ml of methanol at -20°C. The product was collected by filtration, washed with cold methanol and dried under a stream of air then under vacuum overnight (3.20 g, 77%).

^{1}H-NMR (500MHz, C_6D_6): δ_H 7.751(d, 1H *J* = 1.0 Hz, Ar-H), 7.667(dd, 2H *J* = 7.9 & 7.9 Hz, Ar-H), 7.611(d, 1H *J* = 1.2 Hz, Ar-H), 7.57-7.53(m, 3H, Ar-H), 7.521(d, 2H *J* = 8.6 Hz, Ar-H), 7.384(dd, 1H *J* = 7.9 & 1.0 Hz, Ar-H), 7.237(dd, 4H *J* = 8.1 & 8.1 Hz, Ar-H), 7.196(d, 2H *J* = 8.6 Hz, Ar-H), 7.12-7.05(m, 6H, Ar-H), 6.908(dd, 4H *J* = 8.2 & 1.4 Hz, Ar-H *overlapping solvent peak*), 2.116(brm, 4H, octyl-α-CH_2s)*overlapping* 2.074(s, 3H, Me), 2.015(s, 3H, Me), 1.396(s, 9H, BOC-Me_3), 1.119-0.893(brm, 24H, octyl-CH_2's), 0.760(t, 6H *J* = 7.1 Hz, octyl-Me's).^{13}C NMR (125 MHz, C_6D_6): δ_C 153.84, 152.25, 152.15, 147.81, 145.55, 141.47, 140.77, 139.99, 139.50, 138.71, 138.19, 135.79, 133.15, 130.41, 129.61, 129.38, 128.38, 126.54, 126.35, 125.52, 124.17, 23.99, 121.47, 121.37, 120.72, 120.54, 93.08, 80.34, 55.76, 40.94, 32.09, 30.47, 30.05, 29.56, 29.49, 28.32, 24.35, 22.93, 20.79, 14.26. v_{max}/cm^{-1} (C=O, thin film) 1711.m/z: 1055(M+, 30%), 998(45%), 954(M-BOC+, 100%). m.p.: 86-88°C. Elemental Analysis: Calculated for $C_{66}H_{75}IN_2O_2$ C, 75.12; H, 7.16; N, 2.65. Found C, 75.26; H, 7.16; N, 2.83.

Example 11

Compound 10: *tert*-butyl 4-((4-(9,9-dioctyl-7-(4-(trimethylsilyl)phenyl)-9*H*-fluoren-2-yl)phenyl)(*p*-tolyl)amino)phenyl(*p*-tolyl)carbamate

The product was generated by a Suzuki-Miyura reaction. The reagents **9** (7.0 g, 11.33 mmole) and **6** (6.69 g, 11.33 mmole) were placed in a 250 ml RB flask with toluene (100mls) and Et_4NOH (40 ml, 20Wt%). The combined reaction mix degassed by bubbling N_2 through it for 30 minutes. The catalyst $Pd(PPh_3)_4$ (261 mg, 0.226 mmole) was added and the reaction mix degassed for a further 10 minutes. The reaction mix was then heated to 80 °C for 16 hours, cooled to

ambient temperature and the aqueous phase decanted. The toluene solution was filtered through a pad of silica and the silica washed with toluene. The crude product was recovered by removal of the solvent under vacuum and purified by column chromatography (20cm x 8cm) using toluene. Analytically pure material was recovered by dissolving the product in a minimum amount of ether and adding dropwise to 250 ml of rapidly stirred methanol at 0ºC. The product was recovered by filtration and washed with cold methanol, dries under a stream of air and then overnight under high vacuum.R_f = 0.49 (toluene). Yield 10.92 g(96.2%).

^{1}H-NMR (500MHz, C_6D_6): δ_H 7.79(1H, d *J*=1 Hz, Ar-*H*), 7.73(1H, d *J*=1 Hz, Ar-*H*), 7.68-7.70(3H, m, Ar-*H*), 7.66(1H, d *J*=7.5 Hz, Ar-*H*), 7.61(1H, dd *J*=7.5 & 2.0 Hz, Ar-*H*), 7.53-7.57(3H, m, Ar-*H*), 7.50(2H, d *J*=8.5 Hz, Ar-*H*), 7.19-7.23(4H, m, Ar-*H*), 7.17(2H, d *J*=8.5 Hz, Ar-*H*), 7.09(2H, d *J*=8.5 Hz, Ar-*H*), 7.06(2H, d *J*=8.5 Hz, Ar-*H*), 6.88(4H, brd *J*=7.0 Hz, Ar-*H*), 2.14(4H, m, α-C*H*$_2$), 2.08(3H, s, tolyl-C*H*$_3$), 2.02(3H, s, tolyl-C*H*$_3$), 2.08(9H, s, BOC-(C*H*$_3$)$_3$), 0.94-1.12(24H, m, octyl-C*H*$_2$'s), 0.77(6H, t *J*=7.5 Hz, octyl-C*H*$_3$), 0.25(9H, s, TMS-(C*H*$_3$)$_3$). ^{13}C NMR (125 MHz, C_6D_6): δ_C153.8, 152.18, 152.15, 147.7, 145.5, 142.6, 141.4, 140.91, 140.86, 140.5, 140.2, 139.0, 138.6, 35.9, 135.2, 134.2(Ar-H), 133.1, 130.4(Ar-H), 129.6(Ar-H), 128.4(Ar-H), 128.0(Ar-H), 127.4(Ar-H), 127.1(Ar-H), 126.8(Ar-H), 126.3(Ar-H), 125.5(Ar-H), 124.2(Ar-H), 123.9(Ar-H), 121.9(Ar-H), 121.3(Ar-H), 120.7(Ar-H), 120.6(Ar-H), 80.3, 55.7, 40.9(*C*H$_2$), 32.1(*C*H$_2$), 30.4(*C*H$_2$), 29.6(*C*H$_2$), 29.5(*C*H$_2$), 28.3(BOC-(*C*H$_3$)$_3$), 24.4(*C*H$_2$), 22.9(*C*H$_2$), 20.83(*C*H$_3$), 20.79(*C*H$_3$), 14.3(Si-(*C*H$_3$)$_3$). EI *m/z* 1000.5(M+-H, 4%), 900.4(M$^+$-BOC, 100%). m.p.: 88-89°C. Elemental analysis: Calculated for $C_{69}H_{84}N_2O_2Si$ C, 82.75; H, 8.45; N, 2.80. Found C, 82.96; H, 8.27; N, 3.01.

Example 12

Compound 9: (4-(7-bromo-9,9-dioctyl-9*H*-fluoren-2-yl)phenyl)trimethylsilane

The product was generated by a statistical Suzuki-Miyura reaction. The reagents trimethyl(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)silane, **7** (5.0 g, 18.1 mmole) and 2,7-dibromo-9,9-dioctyl-9*H*-fluorene, **8** (15.9 g, 27.0 mmoles) were placed in a 250 ml RB flask with toluene (100mls) and Et_4NOH (40 ml, 20Wt%). The combined reaction mix degassed by bubbling N_2 through it for 30 minutes. The catalyst $Pd(PPh_3)_4$ (0.416 g, 0.36 mmoles) was added and the reaction mix degassed for a further 10 minutes. The reaction mix was then

heated to 80 °C for 16 hours, cooled to ambient temperature and the aqueous phase decanted. The toluene solution was filtered through a pad of silica and the silica washed with toluene. The crude product was recovered by removal of the solvent under vacuum and purified by column chromatography (20cm x 8cm) using petroleum ether (40-60). R_f : 0.34 (7.35g, 65%).

^{1}H-NMR (500MHz, C_6D_6): δ_H 7.739(1H, d *J*=7.5 Hz, Ar-*H*), 7.64-7.69(4H, m, Ar-*H*), 7.604(1H, dd *J*=8.5 & 1.5 Hz, Ar-*H*), 7.590(1H, d *J*= 7.5 Hz, Ar-*H*), 7.557(1H, d *J*=1.5 Hz, Ar-*H*), 7.495(1H, d *J*=1.5 Hz, Ar-*H*), 7.482(1H, dd *J*=8.5 & 1.5 Hz, Ar-*H*), 1.96-2.02(4H, m, α-C*H*$_2$), 1.05-1.25(20H, m, octyl-C*H*$_2$'s), 0.836(6H, t *J*=7.0 Hz, octyl-C*H*$_3$), 0.674(4H, m, octyl-C*H*$_2$), 0.342(9H, s, Si-(C*H*$_3$)$_3$). ^{13}C NMR (125 MHz, C_6D_6): δ_C 153.5, 151.2, 142.1, 140.7, 140.0, 139.63, 139.54, 134.1(Ar-H), 130.2(Ar-H), 126.8(Ar-H), 126.41(Ar-H), 126.38(Ar-H), 121.8(Ar-H), 121.34, 121.27(Ar-H), 120.28(Ar-H), 55.7, 40.5(α-*C*H$_2$), 32.0(*C*H$_2$), 30.2(*C*H$_2$), 29.46(*C*H$_2$), 29.42(*C*H$_2$), 24.0(*C*H$_2$), 22.9(*C*H$_2$), 14.3(*C*H$_3$), -0.82(Si-(*C*H$_3$)$_3$).m.p.: 81-82°C. EI *m/z* 616.4(M$^+$, 95%), 618.4(M$^+$, 100%), 389.1(M$^+$-octyl$_2$H). Elemental Analysis: Calculated for $C_{38}H_{53}BrSi$ C, 73.87; H, 8.65. Found C, 73.77; H, 8.73.

Example 13

Compound 6: *tert*-butyl 4-((4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) phenyl)(*p*-tolyl)amino)phenyl(*p*-tolyl)carbamate

A 250ml RB flask was loaded with *tert*-butyl 4-((4-bromophenyl)(*p*-tolyl)amino)phenyl(*p*-tolyl)carbamate **5** (12.2 g, 22.45 mmole), bis(pinacolato) diboron (8.6 g, 33.67 mmole), KOAc (6.6 g, 67.0 mmole) and (dppf)$PdCl_2$.CH_2Cl_2 (0.459 g, 0.56 mmole) and placed under nitrogen. Dry degassed DMF (90 ml) was added and the reaction mix heated to 80ºC for 2 hours. To the cooled reaction mix was added H_2O (300mls) and the reaction mix extracted with toluene, 3 x 70 ml. The combined toluene extracts were washed with H_2O, 3 x 50 ml and dried over $MgSO_4$. The volume of the filtrate was reduced to approx 50 ml and the solution filtered through a pad of silica and the silica washed with toluene. The solvent was removed form the filtrate to leave a crude product. The product was purified by column chromatography using DCM as solvent. R_f = 0.39 (DCM). Analytically pure material was recovered by recrystallisation from IPA (12.19 g, 54%).

^{1}H-NMR (500MHz, C_6D_6): δ_H 8.009(2H, d *J*=8.5 Hz, Ar-*H*), 7.154(2H, d *J*=8.5 Hz, Ar-*H*), 7.125(2H, d *J*=8.5 Hz, Ar-*H*), 7.103(2H, d *J*=8.5 Hz, Ar-*H*), 6.986(2H, d *J*=8.5 Hz, Ar-*H*), 6.944(2H, d *J* = 8.5 Hz, Ar-*H*), 6.854(2H, d *J*=8.5 Hz, Ar-*H*), 6.791(2H, d *J*=8.5 Hz, Ar-*H*), 2.021(3H, s, tolyl-C*H*$_3$), 2.001(3H, s, tolyl-C*H*$_3$), 1.363(9H, s, BOC-(C*H*$_3$)$_3$), 1.100(12H, s, pinocolato-(C*H*$_3$)$_4$). ^{13}C NMR (125 MHz, C_6D_6): δ_C153.7, 151.2, 145.22, 145.16, 138.9, 136.7 (Ar-H), 135.2, 133.3, 130.3(Ar-H), 129.6(Ar-H), 128.3, 127.9(Ar-H), 127.4(Ar-H), 125.9(Ar-H), 124.5(Ar-H), 122.1(Ar-H), 83.5, 80.3, 28.3(*C*H$_3$), 24.9(*C*H$_3$), 20.82(*C*H$_3$), 20.77(*C*H$_3$). EI *m/z* 590.4(M$^+$, 6%), 490.3(M$^+$-BOC, 100%). Elemental analysis: Calculated for $C_{37}H_{43}BN_2O_4$ C, 75.25; H, 7.34; N, 4.74. Found C, 75.24; H, 7.40; N, 4.74.

Example 14

Compound 5: *tert*-butyl 4-((4-bromophenyl)(*p*-tolyl)amino)phenyl(*p*-tolyl) carbamate

Under N_2, a solution of NBS (1.94 g, 10.87 mmole) in dry, degassed DMF (10 ml), was added dropwise over 30 minutes to a solution of *tert*-butyl 4-(phenyl(*p*-tolyl)amino)phenyl(*p*-tolyl)carbamate **4** (5.0 g, 10.87 mmole) DMF (20 ml) under N_2 at 0°C. The reaction mix was allowed to stir at 0°C for two hours then the reaction deactivated by addition of H_2O (50 ml). The product was recovered by extraction with EtOAc, 3 x 20 ml, the combined extracts washed with H_2O, brine and then dried over $MgSO_4$. The solvent was removed under vacuum and the product purified by column chromatography. R_f = 0.29 (1:1 DCM:Petroleum Ether). Recrystallisation from petroleum ether generated analytically pure material as a white solid (4.57g, 77%).

^{1}H-NMR (500MHz, C_6D_6): δ_H 7.189(d, 4H *J* = 7.7 Hz, Ar-H), 7.093(d, 2H *J* = 8.8 Hz, Ar-H), 6.92-6.87(m, 6H, Ar-H), 6.705(d, 2H *J* = 8.8 Hz, Ar-H), 2.058(s, 3H, Ar-Me), 2.024(s, 3H, Ar-Me), 1.397(s, 9H, BOC-Me$_3$). ^{13}C NMR (125 MHz, C_6D_6): δ_C153.8, 147.4, 145.1, 145.0, 141.3, 138.9, 135.4, 133.3, 132.4, 130.4, 129.6, 128.3, 127.9, 127.5, 125.4, 125.1, 123.9, 0.4, 28.3, 20.84, 20.77. IR: u CO (neat) 1705 cm^{-1}. m.p.: 112-114°C. *m/z*, 542.1578(M(^{79}Br)$^+$, 20%), 543.1644(M(^{81}Br)$^+$, 20%), 544.1592(MH(^{79}Br)$^+$, 20%), 545.1629(MH(^{81}Br)$^+$, 20%), 487.1038(MH-$C_4H_8^+$, 100%). Elemental analysis: Calculated for $C_{31}H_{31}BrN_2O_2$ C, 68.51; H, 5.74; N, 5.15. Found C, 68.58; H, 5.94; N, 5.17.

Example 15

Compound 4: *tert*-butyl 4-(phenyl(*p*-tolyl)amino)phenyl(*p*-tolyl)carbamate

Buchwald-Hartwig reaction standard conditions. Compounds N-4-bromophenyl-tolylaniline (6.36g, 34.7 mmoles), *tert*-butyl 4-bromophenyl(*p*-tolyl)carbamate (12.57g, 34.7 mmoles) and $Pd(OAc)_2$ (0.156 g, 0.69 mmoles) were placed in a 500 ml RB flask and pumped into a glove-box where NaO^tBu (5.0g, 52 mmoles) was added. A suba seal was placed into the flask, which was removed from the glove-box and the flask charged with 200mls of dry, degassed toluene. Finally $^tBu_3PH^+BF_4^-$ (0.200g, 0.69 mmoles) was added under a counter flow of N_2. The reaction mix was then heated to 80°C for 3 hours. The reaction mixture was deactivated by slow addition of NH_4Cl (5g, excess) then filtered through a pad of silica. The solvent was removed under vacuum and the residue slurried in petroleum ether (40-60). The product was recovered by filtration. Analytically pure material was obtained by recystallisation from IPA (11.58g, 72%).

^{1}H-NMR (500MHz, C_6D_6): δ_H 7.170(2H, d *J*=8.0 Hz, Ar-*H*), 7.131(2H, d *J*=8.0 Hz, Ar-*H*), 7.046(2H, dd *J*=8.5 & 1.0 Hz, Ar-*H*), 6.95-7.00(6H, m, Ar-*H*), 6.858(2H, d *J*=8.0 Hz, Ar-*H*), 6.815(2H, d *J*=8.0 Hz, Ar-*H*), 6.779(1H, tt *J*=8.0 & 1.0 Hz, Ar-*H*), 2.037(3H, s, tolyl-C*H*$_3$), 2.002(3H, s, tolyl-C*H*$_3$), 1.374(9H, s, Si-(C*H*$_3$)$_3$). ^{13}C NMR (125 MHz, C_6D_6): δ_C 153.7, 148.3, 145.64, 145.60, 141.4, 138.2, 135.0, 132.8, 130.2(Ar-H), 129.45(Ar-H), 129.41(Ar-H), 127.3(Ar-H), 125.3(Ar-H), 124.0(Ar-H), 123.5(Ar-H), 122.5(Ar-H), 80.1, 28.2(BOC-(*C*H$_3$)$_3$), 20.74(tolyl-*C*H$_3$), 20.66(tolyl-*C*H$_3$). EI *m/z* 464.2(M^+, 4%), 364.2(M^+-BOC, 100%). Calculated for $C_{31}H_{32}N_2O_2$ C, 80.14; H, 6.94; N, 6.03. Found C, 80.38; H, 6.99; N, 6.17. m.p.: 112-114°C.

Compounds N-4-bromophenyl-tolylaniline and*tert*-butyl 4-bromophenyl(*p*-tolyl)carbamate were made by literature methods [B. A. Brown, S. W. Leeming and R. Williams, *Triarylamine compounds, compositions and devices*, WO2006010555 (A1), **2006**, CAN 144:203501].

Example 16

Devices were assembled with a second example of a triblock copolymer formed from a central F8BT core (**Block D**) and a second attached P3HT unit

(**Block C**). Devices were assembled as in example 1. Devices were formulated as listed in Table 3 and recorded device data is listed in Table 4. The data indicate an improved performance with devices formed using Polymer B over a homopolymer blend after annealing at 160°C for 60 minutes devices 3 and 6.

Table 3: Details of the device formulations for devices made with homopolymer blends of P3HT and F8BT compared with devices assembled using Polymer B (P3HT-F8BT-P3HT triblock copolymer)

Sample Device	P3HT (mg)	F8BT (mg)	Polymer B (mg)	Blend details	Spin speed rpm	Average T nm	Anneal
1	0	0	60.8	in 3mL p-xylene	2000	60-70	none
2	0	0	60.8	in 3mL p-xylene	2000	60-70	160°C 30 min
3	0	0	60.8	in 3mL p-xylene	2000	60-70	160°C 60 min
4	40	20	0	in 3mL p-xylene	2000	60-70	none
5	40	20	0	in 3mL p-xylene	2000	60-70	160°C 30 min
6	40	20	0	in 3mL p-xylene	2000	60-70	160°C 60 min

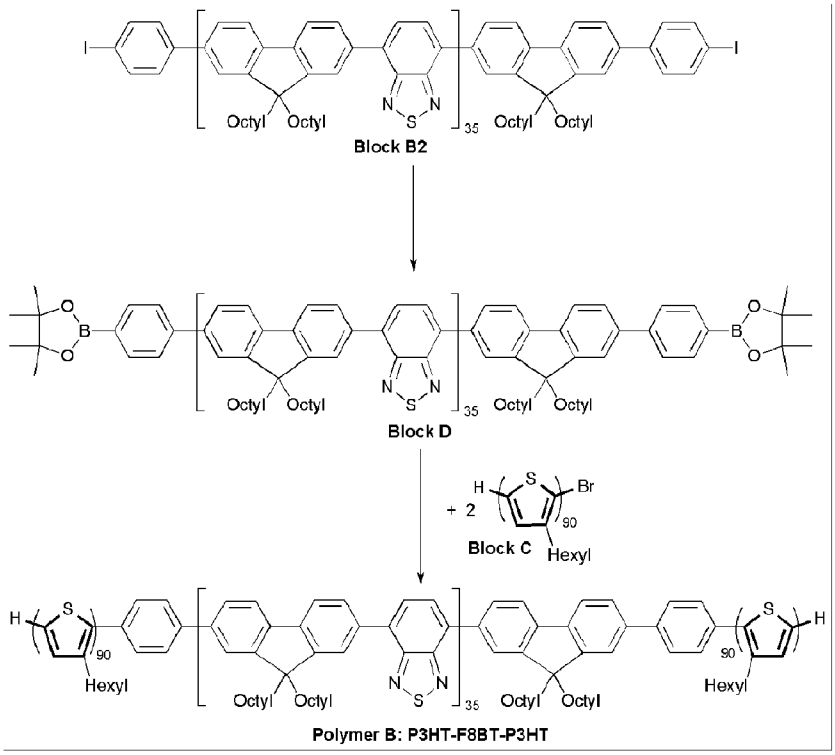
Table 4: Performance data for devices assembled with homopolymer blends of P3HT and F8BT (devices 4, 5 and 6) compared to devices assembled using Polymer B (devices 1, 2 and 3)

Device	Area input	Actual Area (cm2)	Light power (W/cm2)	Voc (V)	Isc (A)	Isc (A/cm2)	FF	Pmax (W/cm2)	V at Pmax	Power Efficiency
1	0.1	0.1	0.1	1.23	1.21E-04	1.21E-03	0.2	3.01E-05	5.44E-01	0.03
2	0.1	0.1	0.1	1.11	1.28E-04	1.28E-03	0.23	3.21E-05	5.44E-01	0.03
3	0.1	0.1	0.1	1.17	1.57E-04	1.57E-03	0.23	4.20E-05	5.54E-01	0.04
4	0.1	0.1	0.1	1.03	1.29E-04	1.29E-03	0.2	2.62E-05	4.54E-01	0.03
5	0.1	0.1	0.1	0.9	1.40E-04	1.40E-03	0.25	3.10E-05	4.64E-01	0.03
6	0.1	0.1	0.1	0.91	1.14E-04	1.14E-03	0.23	2.36E-05	4.44E-01	0.02

Example 17

Synthesis of Polymer B

Scheme 4: Synthetic scheme for the formation of Polymer B, the triblock copolymer P3HT-F8BT-P3HT



Polymer B: Triblock copolymer P3HT-F8BT-P3HT

block-3-hexylthiophene-block-(9,9-dioctyl-9H-fluoren-2-ene)-alt-4,4'-benzo[c] [1,2,5]thiadiazole-block-3-hexylthiophene

A reaction mix containing **Block D** (0.504 g, ≈ 20.6 µmol, M_w 24,500), **Block C** (1.075 g, ≈ 1.33 µmol, M_w15,000), toluene (10mls) and Et_4NOH (20 wt% in H_20, 2 ml) was degassed by bubbling a stream of nitrogen through it for 30 minutes. The catalyst, $Pd(PPh_3)_4$ (5 mg, excess), was added and the nitrogen stream continued for 10 minutes before the reaction mix was stirred at 80°C for 16 hours. The reaction mix was filtered through silica, the volume of the filtrate reduced to 5 ml and the product precipitated by dropwise addition of the toluene

solution to a rapidly stirred MeOH (100mls). The product was collected by filtration, washed with methanol and dried under vacuum. The unreacted P3HT-Br was removed by Soxhlet extraction with cyclohexane. Yield 1.411 g (90 %).

^{1}H-NMR (400MHz, $CDCl_3$): δ_H 7.9-8.1(brm, 8H, F8BT-Ar-*H*), 6.989(s, 8H, Thiophene-Ar-*H*), 2.81(brs, 16H, thiophene-CH_2), 2.18(brs, 4H, F8-α-CH_2), 1.714(brs, 16H, thiophene-CH_2), 1.17-1.45(brm, 88H, C*H*2), 0.922(brs, 24H, thiophene-*Me*), 0.814(brs, 6H, F8-*Me*). ^{13}C-NMR (100MHz, $CDCl_3$): δ_C 154.4, 151.8, 140.9, 139.9*, 136.5, 133.7*, 130.5*, 128.6*, 128.3, 128.0, 124.0, 120.1, 55.5, 40.2, 31.9, 31.7*, 30.5, 30.1*, 30.0, 29.5*, 29.3*, 24.1, 22.66, 22.63*, 14.13*, 14.08. * P3HT Block. Elemental analysis: Calculated $C_{2875}H_{3852}N_{50}S_{225}$ C, 74.53; H, 8.38; N, 1.51. Found C, 75.60; H, 8.47; N, 2.09. GPC (UV-Vis, λ = 325, toluene): M_n 24,500; M_w 46,000; M_p 54,600; M_w/M_n 1.87.

Example 18

Block C: 2-bromo-poly(3-hexylthiophene)

Dry degassed 2-bromo-3-hexylthiophene (2.53 g, 10.2 mmol) was placed in a Schlenk flask under nitrogen and dry, degassed THF (50 ml) was added. The solution was cooled to -40°C followed by slow addition of 1.0 equivalent of LDA (1.0 M solution made by slow addition of BuLi to diisopropylamine in THF at -20°C). The reaction mix was stirred at -40°C for 1 hour and 1.1 eq of $MgBr_2$ added (made by slow addition of dibromoethane to Mg in THF) and the solution warmed to 20°C. The catalyst, (dppp)$NiCl_2$ (90 mg, 0.17 mmol), was added and the reaction allowed to continue until the stirring stopped. The catalyst was deactivated by addition of MeOH (1 ml) and the polymer precipitated by dropwise addition of the reaction mixture to rapidly stirred MeOH (400 ml). The product was recovered by filtration, washed with MeOH and dried under vacuum. The crude product was dissolved in $CHCl_3$, filtered through a pad of silica, the solvent volume reduced and the product precipitated by dropwise addition of the solution to rapidly stirred MeOH. The product was recovered by filtration and washed with MeOH. Yield 0.89 g (53 %). GPC (toluene): M_n 9,500; M_w 15,200; M_p 15,000; M_w/M_n 1.61

The shorter oligomers were removed by recrystallisation, 3 times from cyclohexane.

^{1}H-NMR (500 MHz, $CDCl_3$): δ_H 6.985(s, Th-*H*, 1H), 2.809(brm, Th-α-C*H*$_2$, 2H), 1.711(m, Th-C*H*$_2$, 2H), 1.359(brm, Th-C*H*$_2$, 6H), 0.919(brt, Th-*Me*, 3H).^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 139.9, 133.7, 130.5, 128.6, 31.7, 30.5, 29.5, 29.3, 22.7, 14.1. Elemental analysis: Calculated $C_{900}H_{1261}BrS_{90}$ C, 71.84; H, 8.45. Found C, 73.45; H, 7.83.GPC (toluene):M_n 14,500; M_w 17,400; M_p 15,000; M_w/M_n 1.20

Example 19

Block D: 7,7'-bis((4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl))-poly-(9,9-dioctyl-9H-fluoren-2-ene)-alt-4,4'-benzo[c][1,2,5]thiadiazole

A Schlenk Flask containing **Block B2** (2.48 g, ≈ 0.1 mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (63 mg, 0.25 mmol), KOAc (74 mg, 0.75 mmol) and (dppf)$PdCl_2$.DCM (1.6 mg, 0.002 mmol) was heated at 50°C under vacuum for 1 hour then DMF (20 ml) was added followed by THF (50 ml) to ensure the polymer dissolved. The reaction mix was then stirred at 50°C overnight, cooled and filtered through a pad of silica. The volume of the filtrate was reduced to 20-30mls and the product precipitated by dropwise addition of the solution into rapidly stirred MeOH (400 ml). The product was recovered by filtration, washed with methanol and dried under vacuum. Yield 2.32g (>95%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 7.95-8.10(brm, Ar-*H*, 8H), 7.84* (d, *J* = 7.2 Hz, Ar-*H*, ≈0.25H), 7.11*(d, *J* = Hz, Ar-*H*, ≈0.25H), 7.64*(brm, Ar-*H*, ≈0.25H), 2.80(brs, F8-α-C*H*$_2$'s, 4H), 1.39(s, $BO_2C_2Me_4$, ≈1.1H), 1.16(brm, F8-C*H*$_2$'s, 20H), 0.97(brs, F8-C*H*$_2$'s, 4H), 0.81(brm, F8-*Me*'s, 6H). *end-groups and F8 near chain end. ^{13}C-NMR (100 MHz, $CDCl_3$): δ_C 154.4, 151.8, 140.9, 136.5, 135.3, 133.6, 128.3, 128.0, 126.5, 124.0, 120.1, 55.5, 40.2, 31.8, 30.1, 29.3, 24.9, 24.1, 22.6, 14.1. Elemental analysis: Calculated $C_{1278}H_{1542}B_2N_{70}O_4S_{35}$ C, 80.40; H, 8.14; N, 5.14. Found C, 80.59; H, 8.26; N, 5.02. GPC (UV-Vis, λ = 325, toluene): M_n, 15,800; M_w, 22,400; M_p, 24,500; M_w/M_n, 1.42.

CLAIMS

1. A block copolymer comprising at least one block of electron donor (D) monomer units and at least one block of electron acceptor (A) monomer units wherein at least one of the blocks has a chain length and polydispersity which are controlled within predetermined ranges.

2. The block copolymer of claim 1 wherein at least one of the blocks is conjugated.

3. The block copolymer of claims 1 or 2 wherein said block copolymer is fully conjugated.

4. The block copolymer of any one of claims 1 to 3 wherein said block copolymer is a diblock copolymer.

5. The block copolymer of any one of claims 1 to 3 wherein said block copolymer is a triblock copolymer having a structure ADA, DAD, ADA' or DAD' wherein A and A' represent different electron acceptor blocks and D and D' represent different electron donor blocks.

6. The block copolymer of any one of claims 1 to 5 wherein said block copolymer is free of amphiphilic substituents.

7. The block copolymer of any one of the preceding claims wherein the polydispersity of at least one block is less than or equal to 2.0, preferably less than or equal to 1.5.

8. The block copolymer of any one of the preceding claims wherein the chain length of at least one of the blocks is such that the number average molar mass is between 4,000 and 100,000 Daltons

9. The block copolymer of any one of the preceding claims comprising a first block of controlled polydispersity and at least one other block formed via a chain extension process performed on said first block.

10. The block copolymer of any one of the preceding claims comprising a first block of controlled polydispersity and at least one other block comprising a preformed macromonomeric unit linked to said first block.

11. The block copolymer of claims 9 or 10 wherein the first block is a central block and the said at least one other block is an end block.

12. The block copolymer of any one of claims 1 to 11 wherein the said copolymer assembles in the solid phase in length scales of less than or equal to 100 nm.

13. The block copolymer of claim 12 wherein the said copolymer assembles in the solid phase in length scales from between 15 and 40 nm.

14. The block copolymer of any one of claims 1 to 13 wherein the blocks are based on repeat units selected from the group consisting of linear, branched, fused or linked aromatic, heteroaromatic, arylene vinylene and heteroarylene vinylene.

15. The block copolymer of claim 14 wherein the repeat units comprise a sulphur condensed heterocycle.

16. The block copolymer of claim 15 comprising the monomers triarylamine, 9,9-dioctylfluorene and benzothiadiazole.

17. The block copolymer of any one of claims 1 to 16 wherein the energy level of the highest occupied molecular orbital (HOMO) for the electron donor block is from between -6.5 to -4.5 eV.

18. The block copolymer of any one of claims 1 to 17 wherein the energy level of the highest occupied molecular orbital (HOMO) for the electron acceptor block is below that of the energy level of the highest occupied molecular orbital (HOMO) of the electron donor block and wherein the energy level of the lowest unoccupied molecular orbital (LUMO) for the electron acceptor block is at least

1.0 eV higher than the energy level of the highest occupied molecular orbital (HOMO) of the electron donor block.

19. A method of preparing a conjugated block copolymer comprising providing a first block of controlled polydispersity and chain extending the said first block.

20. A method of preparing a conjugated block copolymer comprising providing a first block of controlled polydispersity and coupling at least one end of said first block a preformed macromonomeric unit.

21. The method of claim 19 or 20 wherein the polydispersity of the central block is controlled through polymerisation.

22. The method of claim 21 wherein the polymerisation technique is selected from the group consisting of controlled living or quasi living polymerisation, quasi living Suzuki polycondensation or living free radical polymerisation.

23. The method of claims 19 or 20 wherein the polydispersity is controlled through physical separation.

24. The method of claim 23 wherein the physical separation is achieved by solubility difference or chromatography.

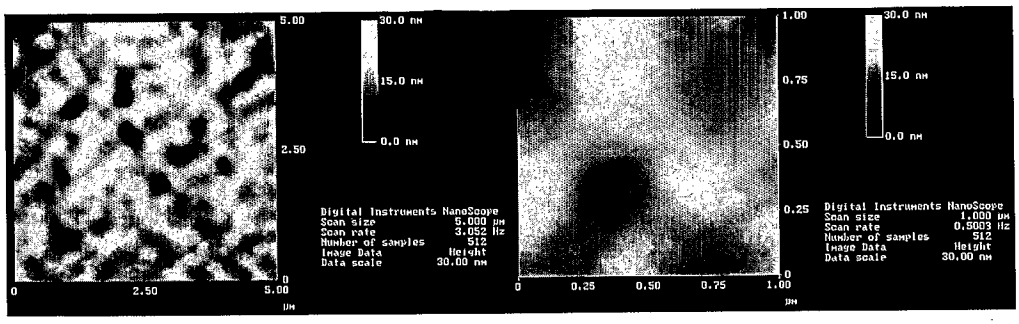
25. A heterojunction device comprising as an active component one or more copolymers of any one of claims 1 to 18.

26. The heterojunction device of claim 25 further comprising one or more electron donors or electron acceptors.

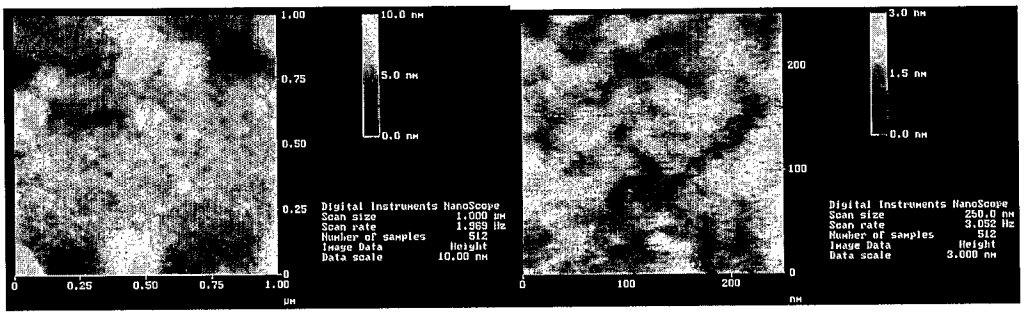
27. A photovoltaic cell comprising a heterojunction device according to claims 25 or 26.

28. Use of the device of claims 25 or 26 in the generation of solar power.

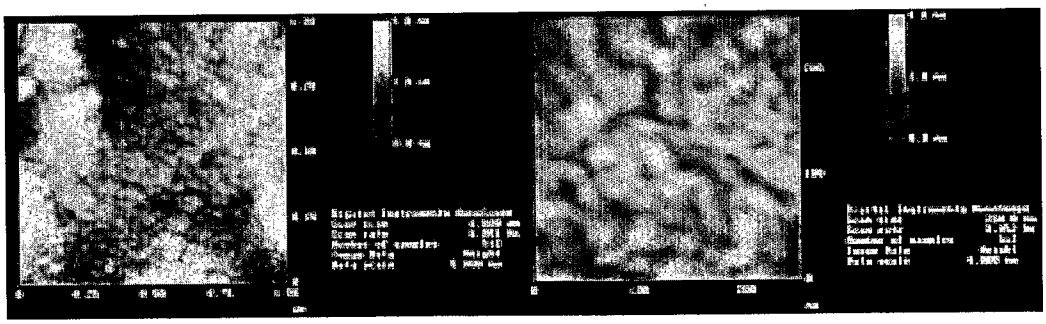
Figure 1



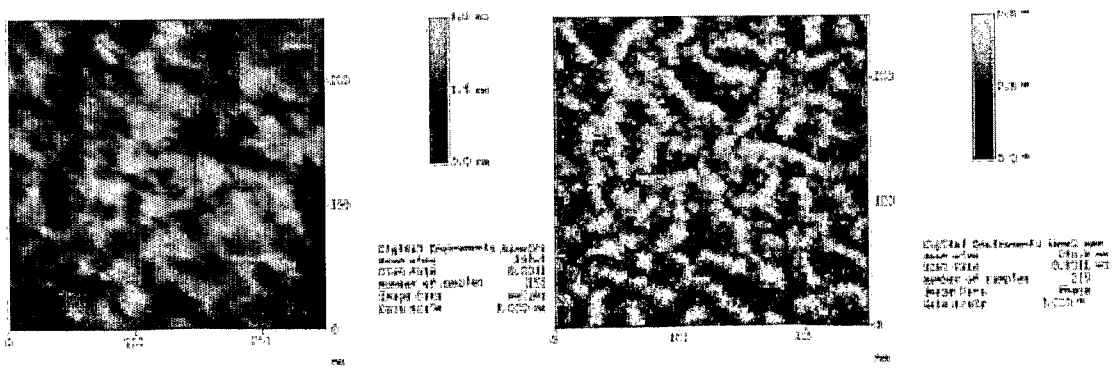
(a) (b)



(c) (d)



(e) (f)



(g) (h)

Figure 2

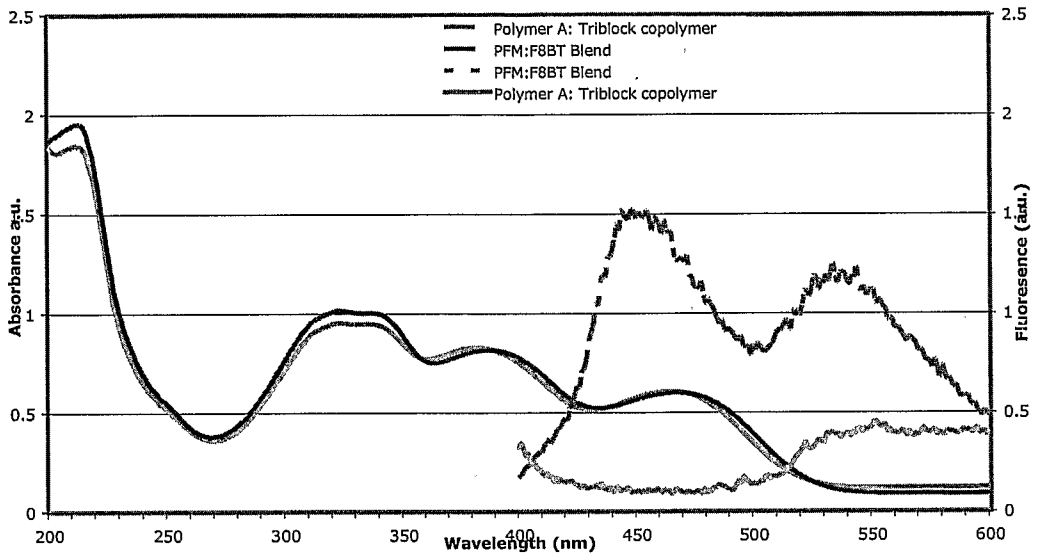

Polymer A: Triblock copolymer
PFM:F8BT Blend
PFM:F8BT Blend
Polymer A: Triblock copolymer
Absorbance a.u.
Fluoresence (a.u.)
Wavelength (nm)
2.5
2
1.5
1
0.5
0
200
250
300
350
400
450
500
550
600

Figure 3

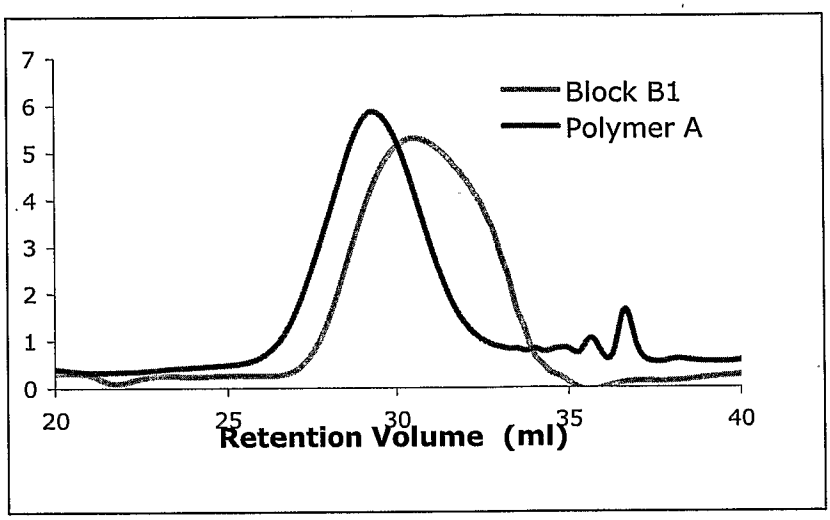
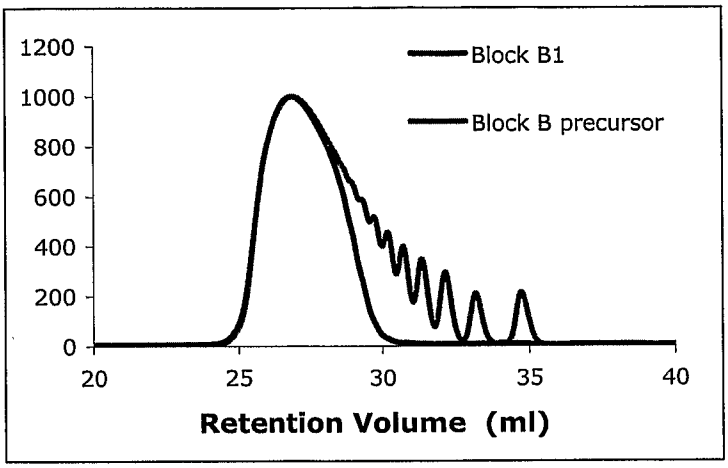

7
6
5
4
3
2
1
0
20
25
30
35
40
Retention Volume (ml)
Block B1
Polymer A

Figure 4


1200
1000
800
600
400
200
0
20
25
30
35
40
Retention Volume (ml)
Block B1
Block B precursor

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2009/001562

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.

C08G 81/00 (2006.01)	***C08G 61/12*** (2006.01)	***H01L 51/30*** (2006.01)
C08F 28/06 (2006.01)	***H01L 31/00*** (2006.01)	***H01L 51/40*** (2006.01)
C08F 228/06 (2006.01)	***H01L 51/00*** (2006.01)	***H01L 51/42*** (2006.01)
C08G 61/00 (2006.01)	***H01L 51/05*** (2006.01)	

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WPI, EPODOC, CAPLUS : (Block Copolymer, Electron Donor, Electron Acceptor, LUMO, HOMO, Sulphur Condensed Heterocycle, Triarylamine, Dioctylfluorene, Benzothiazole, Controlled Living Free radical, RAFT, Nitroxide Mediated and Suzuki Polymerisation, ATRP, Polydispersity)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SCHERF, U., *et al.* "All-Conjugated Block Copolymers," Accounts of Chemical Research, (September) 2008, 41(9):1086-1097. (page 1086, abstract, column 1, lines 4-10, column 2, line 10; page 1087, column 1, lines 10-13 and 19-23, column 2, line 5-7; page 1088; page 1089, column 1, line 3; page 1090, column 1, line 8, column 2, lines 3-4; page 1091, column 1, line 15, column 2, lines 1 and 5-9; page 1095, column 1, lines 13-14; page 1096, column 1, lines 6-11 and 14-21, column 2, lines 2-3)	1-28

[X] Further documents are listed in the continuation of Box C [X] See patent family annex

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 January 2010	08 FEB 2010
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. +61 2 6283 7999	Authorized officer **BALAJI RENGARAJAN** AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No : +61 3 9935 9648

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2009/001562

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2007/070395 A2 (NORFOLK STATE UNIVERSITY) 21 June 2007 (abstract, page 9, column [0012]; page 11, [0015]; page 12, column [0016]; page 18, column [0042]; page 19, column [0044]; page 21, columns [0045]-[0046]; page 23, column [0049]; page 26, column [0053]; claims 1-12 and fig 11)	1-28
X	US 2002/0045719 A1 (HAWKER et al) 18 April 2002 (page 1, columns [0001]-[0002]; page 2; page 3, column [0040]; page 4; page 5, column [0053]; page 7, column [0071], lines 18-19, column (0071], lines 16-18, columns [0073] and [0077])	1-28
X	TU, G., *et al.* "Conjugated Triblock Copolymers Containing Both Electron-Donor and Electron-Acceptor Blocks," Macromolecules, 2006, 39:4327-4331. (abstract; page 4327, column 2, lines 1-5, 25-26 and 17-34; page 4328, column 1, lines 55, 58 and 68-70; column 2, lines 2, 3, 12-15, 18, 27-30, 34, 35, 45, 46, 65 and 66; page 4329, column 1, lines 1-2 and 6; page 4330, column 2, lines 1-9, 16-18 and 35-38; page 4331, column 1, lines 5-13)	1-28
P, X	WOODY, K. B., "Synthesis of All-Conjugated Block Copolymers by Controlled Chain-Growth Condensation Polymerisations," ACS Organic Division, Organic Letters/Essays, (October) 2009, Retrieved from the Internet : <URL: http://organicdivision.org/essays_2009/Woody.pdf>.. (page 1, column 1, lines 5-9, column 2, line 8; page 2, column 1, line 42, column 2, line 11; page 3, column 1, lines 3-5, 12, 19 and 25-26, column 2, lines 6 and 8-9; page 4, column 2, line 31).	1-28

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/AU2009/001562

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
WO	2007/070395	AU	2003287659	CN	1711647	US	2004/0099307
		US	2007/0095391	US	2008/0017244	US	2009/0084444
		WO	2004/047185				
US	2002/045719	US	6355756	US	6433115	US	6512070
		US	2001/0024738				

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

END OF ANNEX