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PAPER

The tuning of the energy levels of dibenzosilole copolymers and applications in organic electronics[†]

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An understanding of the structure-function relationships of conjugated polymers is an invaluable resource for the successful design of new materials for use in organic electronics. To this end, we report the synthesis, characterisation and optoelectronic properties of a range of new alternating copolymers of dibenzosilole. Suzuki polycondensation reactions were used to afford a series of eight conjugated materials by the respective combination of either a 3,6- or 2,7-linked 9,9-dioctyldibenzosilole with 3,6-linked-N-octylcarbazole, triarylamine, oxadiazole and triazole monomers. The copolymers were fully characterised using ¹H, ¹³C{¹H} NMR spectroscopy, size exclusion chromatography (SEC), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The photophysical properties were determined using UV-Vis spectroscopy, photoluminescence (PL) measurements, cyclic voltammetry (CV) and photoelectron emission spectroscopy in air (PESA). The spectroscopic and electrochemical measurements were used to determine the materials' HOMO and LUMO energies and the values were correlated with the copolymer composition and structure. A selection of the copolymers (P4, P5 and P8) were evaluated as the active layer within single-layer polymer light emitting diodes (PLEDs), with the configuration: glass/ITO/PEDOT:PSS/emissive layer/Ba/Al, which gave low intensity electroluminescence. The selected copolymers were also evaluated as the organic semiconductor in bottom-gate, bottom-contact organic field effect transistors (OFETs). The best performing devices gave a maximum mobility of 3×10^{-4} cm² V⁻¹ s⁻¹ and on/off current ratios of 10⁵.

Introduction

Ever since the first reports of a conjugated polymer as the active layer in a light emitting diode (PLED),¹ the potential to use polymers to replace conventional inorganic silicon-based electronics has attracted significant attention.²⁻¹² Conjugated polymers are now also applied in field effect transistors (FETs),^{13,14}

photovoltaics (PV)¹⁵ and chemical sensors.¹⁶ The first commercially available small molecule (O)LEDs are now found in several small-display applications, such as mobile phones and MP3 players. They offer several desirable attributes, such as high resolution and high contrast images, with fast response times and wide viewing angles. In addition to these properties, PLED technology promises to deliver flexible, low cost and ink-jet printable large area displays. There is still much scope for improvement in the performance of materials for organic electronic applications; in particular, some device stabilities and lifetimes are low.^{17,18} It is therefore important that both the semiconducting materials and the understanding of their structure–property relationships continue to be improved.

Within the PLED arena, dialkyl-substituted polyfluorenes are the work-horse materials, due to their efficient blue electroluminescence, high charge carrier mobility and good processability. Fluorene-based moieties are also amenable to a wide range of coupling chemistries and are often used as building blocks. However, the rapid loss of intensity in blue emission, coupled with the appearance of emission bands at lower energies (originating from keto-defect formation at the bridgehead position) during device operation,^{17–20} has led to a significant research effort to replace the bridgehead carbon with a heteroatom.

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The use of heteroaromatic repeat units in conjugated polymers has proved successful for controlling both the polymer energy levels and the stability of the resulting electronic devices.^{6,8–10,21} Silicon is an attractive choice, as its tetravalency allows the introduction of two solubilising substituents per repeat unit, while studies of siloles have shown the potential for enhanced electron transport.^{22,23} Density functional theoretical studies of the silole frontier molecular orbitals indicated an interaction between the butadiene π^* orbital and the silvlene σ^* orbital,²² which predicts the lowered LUMO levels observed in silole systems. In 2005, our research group reported the synthesis of poly(9,9-dioctyl-2,7-dibenzosilole) and its efficient and stable blue electroluminescence.²⁴ The LUMO energy of this material was lowered by approximately 0.1 eV in comparison with poly(9,9-dioctylfluorene). The enhanced thermal stability compared with poly(9,9-dioctyl-2,7-fluorene) was particularly attractive as the latter material is known to undergo degradation under device operating conditions, leading to blue-green emission. Recently, dibenzosilole-containing materials have been used in several applications including OPV,^{25,26} OFET^{27,28} and even as sensors for explosive particulates.^{16,29,30}

In 2005 both our group and that of Cao synthesised poly(9,9dialkyl-3,6-dibenzosilole) homo-polymers.^{31,32} The material reported by Cao and co-workers was formed by a nickel-catalysed coupling reaction and was noted to possess a wide HOMO– LUMO gap of approximately 4.0 eV.³² Our group prepared an end-capped poly(9,9-dialkyl-3,6-dibenzosilole) homo-polymer, *via* a Suzuki polycondensation, which was highly soluble in common organic solvents.³¹ The high energy gap of this material (calculated to be 3.5 eV) was put to use as a host material for a phosphorescent iridium guest complex. The resulting blend was used as the active layer within a green emitting PLED device which displayed efficient electrophosphorescence with a low turn-on voltage (4 V) and complete energy transfer to the guest complex.

A statistical copolymer containing 10% 9,9-dialkyl-3,6-dibenzosilole and 90% 9,9-dialkyl-2,7-fluorene subunits gave pure blue emission, a high external efficiency (3.34%) and a reasonably low turn-on voltage of 6.7 V.³³ A range of copolymers, incorporating 9,9-dialkyl-3,6-dibenzosilole, were recently published by Mo *et al.*, from which PLED devices were prepared. The devices gave predominantly blue or blue/green emission, with external quantum efficiencies of up to 3.17%.³⁴

A recent paper by Xu and Li used a dibenzosilole core in some highly emissive trimeric materials, featuring a methoxysubstituted dibenzosilole core connected *via* ethyne linkages to a phenyl end group.³⁵ Devices were not fabricated with the dibenzosiloles, but all three materials exhibited blue fluorescence with high fluorescence quantum yields (between 0.75 and 0.89).

Marks and co-workers have reported the use of two copolymers of 9,9-dialkyl-2,7-dibenzosilole and thiophene subunits for OFET applications. One material was an alternating copolymer, while the other contained two thiophene moieties within the repeat unit. Both materials showed excellent stability, but low hole mobility values within an OFET device. Within OTFT devices, both copolymers were found to be p-channel materials; the alternating copolymer showed a moderate hole mobility, while the material containing a higher proportion of thiophene showed a high mobility of 6.0×10^{-3} cm² V⁻¹ s⁻¹.^{27,28} Cao and co-workers have recently reported OPV devices with power conversion efficiencies of up to 3.15%, using a blend of PC₇₁BM with two copolymers of 9,9-dioctyl-2,7-dibenzosilole and triarylamine subunits, with different pendant groups attached.³⁶ Yang and co-workers have achieved remarkable power conversion efficiencies (up to 5.1%) in OPV devices using PC₇₀BM blends of polymers and copolymers of dithieno[3,2*b*:2',3'-*d*]silole, a close analogue of dibenzosilole.^{37,38} Examples of dithienosiloles have also been reported as materials for OFETs²⁸ and OLEDs.³⁹

These successes highlight the promise of silicon-containing heteroaromatics for electronic applications. We were therefore interested in further investigation of the properties of various dibenzosilole-containing copolymers. Here we wish to report the preparation of a series of 2,7- and 3,6-linked dibenzosilole alternating copolymers. The influences of the linkage site of the dibenzosilole, along with the nature of the co-monomer, on the copolymer's frontier orbital energies were investigated. Manipulation of the energy levels of these materials in a predictable manner is possible by the judicious choice of both co-monomer and linkage sites of the dibenzosilole repeat unit. The copolymers which were evaluated showed potential for use in PLED/OFET devices.

Results and discussion

A series of eight copolymers was synthesised, four using the 3,6-linked dibenzosilole monomer **1** and four using the 2,7-linked dibenzosilole monomer **2** (see Fig. 1). Oxadiazole and triazole monomers were selected to facilitate electron-transport,^{40,41} whilst carbazole and triarylamine monomers were selected to improve hole-transport.⁴²⁻⁴⁴

Monomer syntheses

The co-monomers 3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-9,9-dioctyldibenzosilole (1) and 3,6-dibromo-Noctylcarbazole were synthesised following literature routes.^{31,45} Synthesis of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2yl)-9,9-dioctyldibenzosilole (2) was performed following a modification to the previously published route which enabled higher vields (two-fold increase) and facilitated scale-up (Scheme 1).²⁴ The Ullmann coupling of commercially available 2,5-dibromonitrobenzene produced the biphenyl 3 in 79% yield. Compound 3 was reduced, with tin powder and HCl, to afford the diamine 4, in 92% yield. Classical diazotization conditions, followed by Sandmeyer reaction (HCl, NaNO₂, KI) afforded the diiodide 5, in 58% yield; a significant improvement on the 30% previously reported.²⁴ The formation of the dibenzosilole 6 from the diiodide 5 proceeded via a selective double halogen-lithium exchange, carried out at -90 °C to ensure selectivity for the iodine substituents. The dilithiated intermediate was treated with di-n-octyldichlorosilane to afford the dibenzosilole 6, in 81% yield. The borylation of 6, using tert-BuLi and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaboralane, enabled the isolation of monomer 2, in 57% yield.

The synthesis of the triarylamine monomer **7** was achieved in a one-step process, utilising a ligand-catalysed Ullmann condensation.^{46,47} 1,10-Phenanthroline monohydrate and copper



Fig. 1 Dibenzosilole copolymers, arranged by dibenzosilole linkage positions.

chloride were used as the catalyst system to couple one equivalent of 4-sec-butylaniline with two equivalents of 4-bromoiodobenzene. The triarylamine 7 was recovered, after extensive purification by column chromatography and recrystallisation, in 33% yield (Scheme 2).

The monomers 2,5-bis(3-bromophenyl)-1,3,4-oxadiazole (9) and 3,5-bis(3-bromophenyl)-4-(4-(octyloxy)phenyl)-1,2,4-triazole (11) were prepared by the condensation of 3-bromobenzoyl chloride with hydrazine monohydrate to afford the hydrazine intermediate 8, in 78% yield. Treatment of 8 with phosphorous oxychloride gave oxadiazole 9, in 88% yield. Treatment of 8 with phosphorous pentachloride, in toluene, afforded the hydrazine 10, in 18% yield. The yield was low due to formation of a large proportion of oxadiazole 9 by-product (approx. 1 : 3 ratio of oxadiazole : hydrazine), as reported in a 1906 study.⁴⁸ The reaction of 10 with 4-octyloxyaniline in *N*, *N*-dimethylaniline, followed by treatment with HCl, afforded monomer 11, in 66% yield (Scheme 3). The crystal structures of 7 and 11 were obtained by single crystal X-ray diffraction (details included in the ESI[†]).



Scheme 1 Synthesis of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-9,9-dioctyldibenzosilole (2). [*Reagents and conditions:* (i) Cu, DMF, 125 °C, 3 h, 79%; (ii) Sn, HCl, EtOH, 100 °C, 2 h, 92%; (iii) HCl, NaNO₂, MeCN, H₂O, -10 to -5 °C, 1 h then KI 60 °C, 16 h, 58%; (iv) *tert*-BuLi, Si (C₈H₁₇)₂Cl₂, -90 °C, 81%; and (v) *tert*-BuLi, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaboralane, -78 °C, 57%].



Scheme 2 Ligand-catalysed Ullmann coupling to form *N*,*N*-bis(4-bromobenzene)-4-*sec*-butylaniline (7).^{46,47} [*Reagents and conditions*: (i) CuCl, 1,10-phenanthroline monohydrate, KOH, toluene, reflux 16 h, N₂, 33%].

Copolymer syntheses

Suzuki polycondensation reactions were used to prepare the eight alternating copolymers (Fig. 1). For each copolymerisation, reaction conditions were identical; the two monomers were added in a 1:1 molar ratio; $Pd(OAc)_2$ and tricyclohexy-lphosphonium tetrafluoroborate were used as the pro-catalyst and pro-ligand respectively; a biphasic mixture of toluene and aqueous tetraethylammonium hydroxide was stirred, vigorously under nitrogen, at 110 °C (Scheme 4). End-capping was achieved by addition of further catalyst/ligand, firstly with bromobenzene and finally with phenylboronic acid, in a 1:2 molar ratio. After filtration through silica, the organic layer was concentrated and precipitated by addition of methanol, filtered and collected. The solid was then re-dissolved in dichloromethane and the precipitation/filtration process was repeated.

Some of the properties of the copolymers are summarised in Table 1. The isolated yields were all reasonably high, ranging from 88% to 96%, showing that the copolymers were not significantly fractionated during work-up. However, the molecular weights were universally low, particularly for copolymers containing the oxadiazole and carbazole monomers, with no increase observed for longer reaction times, using these conditions. The molecular weight may, therefore, be solubility-limited. The polydispersity indices (PDI) determined by SEC were quite narrow for all samples, probably due to the low molecular weights.

Copolymers P6, P1, P3 and P4 exhibited bimodal (and even trimodal) molecular weight distributions by SEC (Table 1 lists the M_{w-max} , the complete distributions are illustrated in the ESI (Fig. S8–S15†)). The cause of this has not been confirmed, but could be due to the relatively low degrees of polymerisation, poor

solubility of the copolymers in the SEC mobile phase (THF), or the formation of macrocycles. The glass transition temperatures, as measured by DSC, ranged from 67–111 °C. This is comparable to the reported T_g values for poly(3,6-dibenzosilole-*co*-2,7-fluorene)-based copolymers (*cf.* 58 °C < T_g < 80 °C).³³ The decomposition temperatures, which were taken as the temperature at which a 5% mass loss occurred, were measured by thermogravimetric analysis and were between 320 and 380 °C, apart from **P5**, which decomposed at 185 °C.

Characterisation and photophysical measurements

The UV-Vis spectra of copolymers **P1** to **P8** were determined in chloroform solutions (Fig. 2). All the materials absorbed in the UV-blue region of the electromagnetic spectrum, the absorption maxima (λ_{max}) and difference between the absorption maxima of the 3,6- and 2,7-linked dibenzosiloles ($\Delta\lambda$) are summarised in Table 2. The 3,6-linked copolymers (**P1–4**) showed absorption maxima and onset wavelengths which were hypsochromically shifted compared to the 2,7-linked copolymers (**P5–8**).

The optically determined HOMO-LUMO gap (E_g) was calculated for each copolymer from the approximated onset wavelength of the absorption $(0 \rightarrow 0)$ band edge (λ_{onset}). The values are summarised in Table 2, together with the difference in energy gap (ΔE_g) between the 3,6-linked dibenzosilole copolymers and their 2,7-linked counterparts (*i.e.* $\Delta E_{g} = \Delta E_{g}$ (3.6) – ΔE_{g} (2,7)). The alternating copolymers of 3,6-dibenzosilole all showed higher energy gaps than the 2,7-substituted analogues, consistent with the previous findings for the two homopolymers.^{24,31,32} Copolymers containing triarylamine (P4 and P8) and carbazole (P1 and P5) subunits have higher absorption onset wavelengths and consequently smaller energy gaps, implying a greater degree of conjugation within these materials. When considering the difference in optical energy gap (ΔE_{g}), observed when the dibenzosilole is linked through '2,7'- or '3,6'-positions, the data show an increase with co-monomer in the order: triarylamine < carbazole < oxadiazole < triazole. An average ΔE_{g} value of 37 nm (0.35 eV) is observed.

The differences in the energy gaps (and hence changes in effective conjugation) for the copolymers can be rationalised by considering the maximum number of conjugated *para*-phenylene units within each polymer backbone. Fig. 3 shows a 'cartoon'



Scheme 3 Synthesis of 2,5-bis(3-bromophenyl)-1,3,4-oxadiazole (9) and 3,5-bis(3-bromophenyl)-4-(4-(octyloxy)phenyl)-1,2,4-triazole (11). [*Reagents and conditions*: (i) *N*-methyl-2-pyrrolidinone, $N_2H_4 \cdot H_2O$, 0 °C to RT 16 h, N_2 , 78%; (ii) POCl₃, 130 °C, 7 h, N_2 , 88%; (iii) PCl₅, toluene, reflux, 16 h, 18%; and (iv) *N*,*N*-dimethylaniline, 135 °C, 48 h, 66%].



Scheme 4 General reaction scheme for Suzuki polycondensations. [*Reagents and conditions*: (i) 2 mol% Pd(OAc)₂, 8 mol% [(C_6H_{11})₃PH] BF₄, 20% aq. (C_2H_5)₄NOH, 110 °C, 48 h; (ii) bromobenzene, 2 mol% Pd(OAc)₂, 8 mol% [(C_6H_{11})₃PH] BF₄, 110 °C, 16 h; and (iii) phenylboronic acid, 2 mol% Pd (OAc)₂, 8 mol% [(C_6H_{11})₃PH] BF₄, 110 °C, 16 h; and (iii) phenylboronic acid, 2 mol% Pd (OAc)₂, 8 mol% [(C_6H_{11})₃PH] BF₄, 110 °C, 16 h; and (iii) phenylboronic acid, 2 mol% Pd (OAc)₂, 8 mol% [(C_6H_{11})₃PH] BF₄, 110 °C, 16 h].

Table 1 Physical properties of copolymers P1-P8

Copolymer		P1	P2	P3	P4	P5	P6	P7	P8
Dibenzosilole Co-monomer Isolated yield	М	1 CBZ 96% 4800	1 9 89% 3300	1 11 94%	1 7 92% 8000	2 CBZ 96% 3400	2 9 88% 4000	2 11 91% 6700	2 7 92% 5700
DSC ^b TGA ^c	$M_{\rm w}$ $M_{\rm w}$ PDI $T_{\rm g}/^{\circ}C$ $T_{\rm d}/^{\circ}C$	4800 6600 1.38 76 343	5600 1.7 90 380	10 500 1.52 107 363	10 700 1.34 84 328	5500 1.61 87 185	4000 4700 1.19 67 347	12 200 1.82 111 332	11 700 2.05 90 353

^{*a*} SEC measurements were carried out in THF using narrow molecular weight polystyrene standards as the calibrant. ^{*b*} DSC analyses were conducted at a scan rate of 40 °C min⁻¹. In each case, three cycles were recorded and the average value is reported. ^{*c*} The decomposition temperature is reported as the temperature at which 5% weight loss occurred. This was determined using TGA at a scan rate of 10 °C min⁻¹; CBZ—3,6-dibromo-*N*-octylcarbazole.

depiction of a short chain of each of the eight copolymers, arranged by co-monomer and dibenzosilole monomer used. Maximum lengths of conjugation (through *para*-phenylene units) are highlighted in blue, while possible conjugation through other subunits is highlighted in purple.

Within the triarylamine-containing copolymers P4 and P8, overlap between the aryl π -system and the p-orbital of the nitrogen atom leads to a high degree of conjugation along both of these polymer backbones (highlighted in purple). In the case of P8, the length of conjugation is essentially 'non-limited' in theory (although in reality, steric interactions may limit this conjugation length, by causing rotational distortions and diminishing the orbital overlap). The backbone of copolymer P4 contains



Fig. 2 UV-Vis spectra of the copolymers, recorded in CHCl₃ solution $(\sim 4 \times 10^{-5} \text{ mol dm}^{-3})$ and intensity-normalised.

meta-linkages, however, which limit the possible length of conjugation to either 2 or 5 phenylene units (highlighted in blue). Since the change in orbital energy gap between these two systems is not particularly large, it can be inferred that the effective conjugation length in polymer **P8** is therefore slightly longer than 5 phenylene units. The increased conjugation in these polymers leads to a decreased energy gap and an increased UV-Vis absorption onset wavelength (the highest amongst the eight copolymers).

When considering the carbazole-containing systems **P1** and **P5**, some degree of conjugation is expected to exist (as with the triarylamines) between the aryl π -system and nitrogen p-orbital.^{45,49} Since the UV-Vis absorption onset wavelength of **P5** is within 2 nm of that of copolymer **P4**, the effective conjugation of the (theoretically, non-limited) copolymer **P5** must also be around 5 phenylene units. This indicates that the extent of conjugation through a 3,6-linked carbazole subunit is lower than that though a triarylamine subunit. Accordingly, the onset wavelengths are lower for carbazole-containing copolymers.

When considering the oxadiazole- and triazole-containing copolymers, it can be seen from Fig. 3 that **P6** and **P7** both have maximum conjugation lengths of 3* and 4 units (where * denotes an unknown extent of conjugation over the triazole/ oxadiazole 5-membered rings). The maximum conjugation length for both materials is therefore predicted to be the same 4-unit stretch along the dibenzosilole subunit. This postulation is supported by identical UV-Vis onset wavelengths for each

 Table 2
 Summary of UV-Vis absorption onset wavelengths of copolymers P1 to P8, along with calculated differences in wavelengths and band gap energy

		Wavelength λ/nm			
Measurement	Co-monomer	2,7-Dibenzosilole, E_{g}/eV^{-1}	3,6-Dibenzosilole, E_{g}/eV^{-1}	Δλ/nm	$\Delta E_{\rm g}/{\rm eV}$
UV-Vis absorption maximum, λ_{max}	Triarylamine	P8 : 390	P4 : 353	37	_
1 / max	Carbazole	P5 : 353	P1 : 296	57	
	Oxadiazole	P6 : 320	P2 : 268	52	
	Triazole	P7 : 326	P3 : 268	58	
UV-Vis onset. λ_{onset}	Triarvlamine	P8 : 428 (2.90)	P4 : 400 (3.10)	28	0.20
onset	Carbazole	P5 : 398 (3.12)	P1 : 366 (3.39)	32	0.27
	Oxadiazole	P6 : 364 (3.41)	P2 : 328 (3.78)	36	0.37
	Triazole	P7 : 364 (3.41)	P3 : 312 (3.97)	52	0.56

material, with a value of 364 nm (giving an energy gap of 3.41 eV). The 3,6-linked copolymers P2 and P3 do not have the same 4-unit maximum conjugation lengths, as the linkages are now '*meta*'; the oxadiazole/triazole subunits must therefore be the maximum conjugation lengths (3^* units). Since the onset wavelength is lower for P3 than for P2, it can be concluded that the oxadiazole subunit is more highly conjugated than the triazole subunit.

In general, the 3,6-linked dibenzosilole copolymers have lowered frontier orbital energy gaps, as a consequence of the diminished conjugation due to *meta*-linkages. The difference in energy gaps between the 2,7-linked and 3,6-linked systems, ΔE_g , is smaller for the triarylamine and carbazole-containing materials because the interaction of phenylene π -orbitals with nitrogen p-orbitals leads to increased conjugation for both 2,7- and 3,6-linked systems.



Fig. 3 Depiction of maximum conjugation lengths within copolymer backbones. *Note*: †—may not be unlimited due to steric-induced distortional effects; *—denotes an extended conjugation, which may not have the same strength as a biphenyl subunit.

Photoluminescence spectra and cyclic voltammetry

The copolymers were spin-coated onto quartz plates and photoluminescence spectra of the eight thin films were measured, using the absorption maxima values, obtained by UV-Vis spectroscopy, as the excitation wavelength (Fig. 4). The majority of spectra display multiple emission maxima, due to multiple electronic excitations. Most of the samples emit in the violet-blue region of the visible spectrum (the electromagnetic spectrum is shown at the top of the graph for reference), however, the emission maxima for copolymers P1, P2 and P3 lie within the UV region (with P1 and P2 having large shoulder peaks in the blue region). The CIE coordinates of the emission from the eight copolymers, in the thin-film state, were determined from the photoluminescence spectrum from each material and the results are tabulated in Fig. 4. All the copolymers exhibited deep blue photoluminescence, in most cases close to the CIE coordinates for high definition blue LED devices (0.15, 0.06). Only materials P1, P5 and P8 do not give pure blue emission.

The emission spectra were also recorded in solution (chloroform). The majority of the spectra were very similar to the thin films, with the exception of **P1** and **P2**. The appearance of lower energy emission bands in the solid state (thin film) is ascribed to aggregation effects (Fig. 5). Both materials **P1** and **P2** show single emission maxima in solution (as did all of the copolymer samples) and these emission maxima coincide with the maxima present in the solid state.

Cyclic voltammetry was used to determine the frontier orbital energy levels for each copolymer (Table 3). The materials were spin-coated onto a glass-carbon working electrode and immersed, with a platinum wire counter electrode and Ag/AgCl pseudo reference electrode, in a solution of tetrabutylammonium perchlorate in acetonitrile, under argon. Measurements were calibrated using the ferrocene/ferrocenium redox couple as the internal standard. Where available, the oxidation and reduction potentials of the thin films were used, according to the method reported by Thelakkat and Schmidt,⁵⁰ to estimate the HOMO and LUMO levels. Copolymers containing oxadiazole subunits (P2 and P6) and triazole subunits (P3 and P7) gave no observable reduction or oxidation responses. The copolymers containing carbazole and triarylamine repeat units gave irreversible oxidation responses. Some of the copolymers dissolved from the surface of the working electrode, during electrochemical



Fig. 4 PL spectra and calculated CIE coordinates for the copolymer samples spin-coated on quartz plates.



Fig. 5 Comparative PL spectra of copolymers P1 and P2 in the solution and solid states.

measurements. As a result, the oxidations for copolymers P1, P4 and P8 were non-reproducible; for copolymer P8, the oxidation at 0.62 V becomes weaker with successive cycles. For copolymer P4 the peak at 0.62 V decreases, while the shoulder at 0.50 V increases; for copolymer P1 the peak at 0.90 V decreases while the shoulder at 0.70 V increases (Fig. S1–S5†). The cyclic voltammetry measurements are therefore somewhat ambiguous, which may explain the discrepancies with some of the photoelectron spectroscopy in air (PESA) measurements (see later).

The optical energy gaps were calculated from the extrapolated absorption onset wavelengths of the UV-Vis spectra (*vide supra*). Alongside these measurements, the ionisation potential (used as an estimate for HOMO energy) of each of the copolymers was recorded using photoelectron emission spectroscopy in air (PESA). Samples were spin-coated onto glass slides and a Riken-Keiki Co. ACII spectrometer was used to measure the ionisation potentials, according to the method described by Winzenberg *et al.*⁵¹ The orbital energies and E_g obtained using the two methods were similar for all samples, where redox responses were observed. The best correlations were found for the copolymers containing 2,7-dibenzosilole repeat units.

On examination of the derived HOMO–LUMO energy levels, certain trends emerge. Within the group of copolymers containing 3,6-linked dibenzosilole, those materials which include a hole-transporting subunit (P4—triarylamine, P1—carbazole) have a hole-blocking nature, due to low HOMO levels (P4: -5.62 eV; P1: -5.77 eV). Those which include an electrontransporting subunit (P2—oxadiazole, P3—triazole) have an electron-blocking nature, due to high LUMO levels (P2: -1.72 eV; P3: -1.76 eV). It can be seen, therefore, that for 3,6-dibenzosilole copolymers, the transport properties of the material are opposite to the transporting nature of the co-monomer subunit.

This trend is reversed, however, for the copolymer materials containing 2,7-dibenzosilole subunits. For the copolymers containing a hole-transporting subunit (**P8**—triarylamine, **P5**—carbazole), a hole-transporting nature is observed, due to raised HOMO levels (**P8**: -5.43 eV; **P5**: -5.47 eV). For those materials containing an electron-transporting subunit (**P6**—oxadiazole, **P7**—triazole), an electron-transporting nature is observed, due to lowered LUMO levels (**P6**: -2.42 eV; **P7**: -2.53 eV) (Fig. 6).

The copolymers with triarylamine and carbazole repeat units have higher HOMO energies and thus would be expected to show better hole-transport, whilst the copolymer with oxadiazole and

Table 3 Cyclic voltammetry data obtained from reduction and oxidation sweeps performed on spin-cast thin films^a

Copolymer	Dibenzosilole	Co-monomer	Oxidation potential/V	HOMO energy/eV	Reduction potential/V	LUMO energy/eV
P1 ^c	1	3 6-Carbazole	0.72	-5.52	d	d
P2	1	Oxadiazole (9)	d	d	d	d
P3	1	Triazole (11)	d	d	d	d
$P4^c$	1	$Ar_2N(7)$	0.53	-5 33	d	d
P5	2	3.6-Carbazole	0.68	-5.48	d	d
P6	2	Oxadiazole (9)	d	d	d	d
P7	2	Triazole (11)	d	d	d	d
$\mathbf{P8}^{b}$	2	$Ar_3N(7)$	0.56	-5.36	d	d

^{*a*} Note: glass-carbon working electrode. Ag/AgCl pseudo reference electrode, platinum wire counter electrode, 0.1 M tetrabutylammonium perchlorate in acetonitrile, under a blanket of argon. Oxidation sweeps performed at 1000 mV s⁻¹ and used to calculate HOMO energy; reduction sweeps performed at 100 mV s⁻¹ for LUMO energy measurement. ^{*b*} Non reproducible. ^{*c*} Non reproducible, new peak appearing. ^{*d*} Not observed.

triazole could show electron-transport, due to their lowered LUMO energies. Another factor to note is that the 2,7-dibenzosilole copolymers show lower E_g compared with the 3,6-linked counterparts. For a single layer PLED device, with conventional configuration ITO/PEDOT:PSS/anode and LiF/Al or Ba/Al cathode structures, copolymer **P8** would be expected to have the greatest efficiency due to having the lowest barriers for charge injection at both the anode and cathode.

Light emitting diodes (PLEDs)

For each of the different emissive materials, a set of four PLED devices, each with 8 pixels, was prepared with the configuration: glass/ITO/PEDOT:PSS (10 nm)/copolymer P1–P8 (50 nm)/Ba (0.5 nm)/Al (100 nm). In general, there were difficulties processing and encapsulating the copolymers and the films showed a range of defects (pin-hole, comet type) and significant delamination of the active layer. The electroluminescence spectra of copolymers P4, P5 and P8 at a driving voltage of 9 V are shown in Fig. 7. The spectrum for P5 (containing 2,7-dibenzosilole-carbazole repeat units) showed electroluminescence in the blue region, which was slightly red-shifted (~10 nm) compared with the photoluminescence spectrum (Fig. 4). P8 (2,7-dibenzosilole-triarylamine) showed very low intensity electroluminescence in

both the blue and red regions of the spectrum, with the blue emission being dominant.

P4 (3,6-dibenzosilole-triarylamine) showed higher intensity EL, but surprisingly the emission is mainly in the red region of the spectrum, with only a minor blue emission. Table 4 summarises the CIE coordinates and external quantum efficiencies (EQE), while comparing the values with the PL CIE coordinates. Only P5 shows a reasonable agreement between optical and electronic spectra. The other copolymers all showed some red-emission. This was probably due to problems controlling the thickness of emissive layer (in practice, this was potentially far greater than 50 nm) and to the difficulties in obtaining uniform, smooth films with these copolymers. Changes in the emissive layer thickness have been shown to lead to significant changes in device efficiencies and emission colour for polyfluorenes.⁵² These changes can be caused by an optical interference effect within the 'weak microcavity'.53 Changes in film morphology at the point of light emission along with selfabsorption by the emissive material can also have a great effect on the device output. Simulations of emission from a white OLED device have shown that as the zone of emission can affect the out-coupling of different wavelengths of light; with larger distances between cathode and emission zone favouring red light out-coupling.54



Fig. 6 Comparison of copolymer energy levels, as determined by CV measurements and PESA measurements. [Note: E_g determined optically by UV-Vis absorption onset. Dark blue bars are values obtained from CV; light blue from PESA. No CV data for white bars; values from PESA and UV-Vis only.]



Fig. 7 Electroluminescence spectra of copolymers P4, P5 and P8, recorded at 9 V and normalised.

Table 4Summary of the emission properties of the copolymers^a

Copolymer	PL CIE coordinates	Device CIE coordinates	QE factor
P4	[0.16, 0.05]	[0.48, 0.35]	0.006
P5	[0.16, 0.07]	[0.20, 0.15]	0.011
P8	[0.15, 0.10]	[0.26, 0.23]	0.010

 a QE = quantum efficiency, as determined by division of current passing through the device by number of photons detected (at the electroluminescence maximum wavelength).

Field effect transistors (FETs)

In order to determine the charge transport characteristics of the copolymers, organic field-effect transistors (OFETs) were fabricated and tested (Table 5). Only the copolymers with smallest E_g and HOMO levels closest to the work-function of gold (~5.1 eV): **P4**, **P5** and **P8** were selected for investigation.

A bottom-contact, bottom-gate (BCBG) device architecture was employed (inset in Fig. 8(a)) and the OFETs were fabricated on a highly doped silicon substrate, which acted as a common gate electrode. A thermally grown 200 nm layer of silicon dioxide was then used as the gate dielectric. The SiO₂ layer was treated with hexamethyldisilazane (HMDS) in order to improve crystallisation.⁵⁵ Gold source and drain electrodes were patterned using standard photolithography.

Of the copolymers studied for use in OFETs, **P8** showed the best performance, while **P4** and **P5** gave lower mobilities and current on/off ratios (Table 5). The device characteristics for OFET devices fabricated using **P8** show negligible hysteresis and

Table 5 OFET device mobilities and on/off ratios

Copolymer	Linear mobility $\mu/cm^2 V^{-1} s^{-1}$	Saturation mobility $\mu/cm^2 V^{-1} s^{-1}$	Current on/ off ratio
P4 P5 P8	$egin{array}{llllllllllllllllllllllllllllllllllll$	$\begin{array}{c} 2.7\times 10^{-5} \\ 1.1\times 10^{-5} \\ 2.7\times 10^{-4} \end{array}$	10 ³ 10 ³ 10 ⁵



Fig. 8 (a) Transfer characteristics (schematic cross-section inset); (b) output characteristics of **P8**-based bottom-contact, bottom-gate organic field-effect transistor ($L = 10 \ \mu m$ and $W = 20 \ mm$) measured after annealing at 100 °C for 1 hour under ambient pressure N₂.

a large current on/off ratio. Optimum results were achieved when using an annealing temperature of 100 °C. The transfer characteristics (drain current I_D as a function of gate voltage V_G) are shown in Fig. 8(a), while the output characteristics (drain current I_D as a function of drain voltage V_D) are shown in Fig. 8(b). Using standard semiconductor models,⁵⁶ the field effect mobility was determined, from the transfer characteristics, to be approximately 3×10^{-4} cm² V⁻¹ s⁻¹. From plots of $I_D^{1/2}$ against V_G (data not shown) the threshold voltage was determined to be -31 V. The current on–off ratio was estimated to be 10⁵.

Conclusions

A series of eight novel copolymers have been synthesised by Suzuki polycondensation. A significant improvement in the overall yield for the synthesis of 2,7-bis(4,4,5,5-tetramethyl-1,3,2dioxaborolane-2-yl)-9,9-dioctyldibenzosilole (**2**) has been achieved and the synthesis of three novel co-monomers is reported.

The copolymers were fully characterised using a range of spectroscopic and opto-electronic techniques. The UV-Vis spectra were used, in conjunction with cyclic voltammetry and PESA, to derive the frontier orbital energies. A clear pattern was observed in the hypsochromic shift in absorption from 2,7-linked to 3,6-linked dibenzosilole copolymers. As a result, materials containing the 2,7-linked dibenzosilole repeat units had a significantly smaller energy gap than that of the 3,6-linked counterparts. The relative charge transport properties of the copolymers were altered in a predictable manner by the inclusion of either hole- or electron-transporting subunits, and were dependent on the linkage positions within the dibenzosilole sub-unit.

From the photoluminescence measurements and frontier orbital energy levels, all of the copolymer materials showed promise for use as blue OLED emissive materials (often meeting the CIE coordinate specifications for blue emission), with the exception of the UV-emitters P2 and P3. However, the electroluminescence performance of the PLED devices was poor. This is primarily ascribed to the film-forming capabilities of the copolymers. Devices fabricated with copolymers P4 and P8 gave the highest luminance levels and current densities (within the voltage range 8 to 12 V). These materials both feature a triarylamine subunit and exhibit the lowest LUMO levels within the series of copolymers. This suggests that the reduced electron-injection barrier led to improved device performance, which in turn implies that the electron-injection barrier is of more importance than the barrier for hole-injection, for the dibenzosiloles tested and the device architecture employed. The device containing copolymer P4 displayed mostly red emission, while that containing P8 displayed mostly blue emission. It can therefore be envisaged that the higher HOMO level of P8 (-5.43 eV) reduces the hole-injection barrier, leading to improved charge injection balance and increased polaron recombination within the desired zone of emission. In the case of P4, a lowered HOMO level (-5.62 eV) increased the hole-injection barrier, which leads to an unbalanced charge injection and the recombination of polarons closer to the PEDOT:PSS/emissive layer interface than within the desired emission zone.

Carbazole-containing copolymers P1 and P5 afforded devices with lower luminance levels and current densities than those containing P4/P8. Both of these materials feature slightly higher LUMO levels than the triarylamine-containing copolymers (P1: -2.38 eV; P5: -2.35 eV). Accordingly, the electron-injection barrier is increased, leading to the observed decrease in device performance. The device containing copolymer P5 produced the best observable emission profile (Fig. 7), showing a pure blue output, while the device containing P1 produced the lowest intensity and widest emission profile, giving a mixture of blue and red electroluminescence. The higher HOMO level of P5 (-5.47 eV) reduces the hole-injection barrier, thereby improving charge injection balance and resulting in polaron recombination/ emission occurring within the desired emission zone. In the case of P1, however, the lower HOMO level (-5.77 eV) leads to an increased hole-injection barrier and a poor balance of charge injection, hence radiative recombination of polarons will occur predominantly towards the PEDOT:PSS/emissive layer interface.

In contrast with these materials, copolymers containing electron-transporting oxadiazole (P2 and P6) and triazole (P3 and P7) subunits afforded the worst devices, with only the device containing copolymer P6 giving any measurable output. These materials had the highest LUMO (P2 and P3) or lowest LUMO (P6 and P7) levels and therefore the greatest barriers to electronand hole-injection respectively. From within this grouping, copolymer P6 had the most balanced charge injection barriers and the smallest energy gap, due to the 2,7-dibenzosilole subunit, which may explain why it was the only material to give a working device (electroluminescence was observed visually, but was not sufficiently intense to record an EL spectrum).

In light of the promising photoluminescence measurements but modest electroluminescence performances of the dibenzosilole copolymers, further optimisation of polymerisation conditions in order to maximise molecular weight and improve filmforming abilities would be worthwhile and could significantly improve device performances.

Finally, an OFET prepared using **P8** showed good hole mobility and a high current on/off ratio. This promising preliminary result implies that other copolymers incorporating dibenzosilole and hole-transporting subunits could be used in order to raise the peak charge mobility.

Experimental section

General methods

Proton NMR spectra were performed on a Bruker Av-400 (400 MHz), carbon-13 NMR spectra were recorded with proton decoupling on a Bruker Av-400 (100 MHz). Silicon-29 NMR spectra were performed on a Bruker Av-400 (79 MHz). Chemical shifts are reported in ppm relative to residual protons in the commercially available deuterated solvents. All spectra were analysed using MestreNova software, from MestreLab. SEC data were collected using a Polylabs PCL-50, with 2 MIXED-D columns in series at 25 °C, using THF as the eluent and narrow molecular weight polystyrene standards as calibrants. Flash column chromatography was performed on Merck Kieselgel 60 (230-400 mesh) silica. Analytical thin layer chromatography (TLC) was performed on pre-coated 0.25 mm thick Merck 5715 Kieselgel 60 F254 silica gel plates and observed under 254 nm or 366 nm ultraviolet light. Melting points were determined with a Gallenkamp melting point apparatus and are uncorrected. Elemental analyses were performed by Mr Steven Boyer, London Metropolitan University. X-Ray crystallography structure refinements were performed by Dr A. J. P. White, Department of Chemistry, Imperial College London. Photoluminescence spectra were recorded using a Varian Cary Eclipse Fluorescence Spectrometer. Thin films were prepared by spin casting toluene solutions of the copolymers (15 mg in 1 cm^3) on cut microscope slides. UV/Vis spectra were recorded in solution, using a Perkin Elmer LAMBDA 25 spectrophotometer. Infrared absorptions were measured in the solid state (or neat liquid in the case of oil samples) using a Perkin Elmer 400 FT spectrometer. Photoelectron spectroscopy in air (PESA) measurements were made using a Riken Keiki AC-II at Cambridge Display Technology and at CSIRO Materials Science and Engineering. Differential scanning calorimetry measurements were recorded using a Perkin Elmer Pyris 1 DSC instrument with liquid nitrogen as coolant. 10-15 mg of the polymer sample was sealed in an aluminium pan with a crimping tool. The sample was heated from 30 °C to 200 °C at a heating rate of 40 °C min⁻¹, held for 1 minute at 200 °C, then cooled to 30 °C at a rate of 40 °C

min⁻¹. This cycle was repeated three times, then twice more with a heating rate of 100 °C min⁻¹. Thermogravimetric analysis measurements were recorded using a Perkin Elmer Pyris 1 TGA instrument. 5–10 mg of the copolymer sample were loaded into the crucible and accurately weighed. The sample was then heated from 100 °C to 650 °C, under a 20 mL min⁻¹ flow of nitrogen. The decomposition temperature, T_d , was determined by the temperature at which 5% mass loss of the sample occurred. Low resolution mass spectrometry was performed on a VG Autospec Q spectrometer (EI) or an LCT Premier electrospray spectrometer (ESI). High resolution mass spectrometry was performed on a VG Autospec Q spectrometer.

Device fabrication

PLED device fabrication was conducted using an MBraun nitrogen-filled glovebox, within a clean-room environment at Cambridge Display Technology Ltd. Pre-patterned ITO-covered glass plates ($45 \times 45 \times 0.7$ mm) were annealed and UV/ozone cured for 2 min before a 10 nm layer of PEDOT:PSS was deposited by spin-coating (dispense phase-300 rpm (acceleration 100 rpm²) 4 s; spin phase—lid closed, 2610 rpm (acceleration 5000 rpm²) 7 s; dry phase—lid open, 400 rpm (acceleration 100 rpm²) 60 s). The plates were then annealed at 170 °C for 15 minutes and a 50 nm layer of the emissive layer (from the range of copolymers) was spin-coated and dried before briefly annealing at 80 °C. A metal evaporation system, with a shadowmask grille, was used to deposit a 0.5 nm layer of elemental barium, followed by 100 nm of elemental aluminium. The whole device was then encapsulated within a moisture/oxygen impermeable casing, complete with electrical pin contacts attached to the separated electrodes. A purpose-built testing rig was used to automatically analyse the photophysical properties and current/ voltage characteristics of each batch of devices. Spin trials were performed by spinning polymer solutions onto plain 0.7 mm \times 45 mm \times 45 mm glass plates within a glovebox. The sample plates were subsequently removed from the glovebox, scored with a needle and the surface profile measured using a Dectak stylus profiler. The spin trials and device spin-coating for polymer P3 were performed on an open-bowl spinner with a vacuum chuck.

OFETs were fabricated on a proprietary silicon substrate from Philips. After photolithographic patterning of the gold electrodes, a 10 mg mL⁻¹ solution (chlorobenzene) of copolymer was spin-cast onto the substrate, under a nitrogen atmosphere. The sample was annealed for one hour, at 100 °C. Electrical characterisation was carried out using a Keithley 4200 semiconductor parameter analyser, under a nitrogen atmosphere.

Materials

Unless otherwise stated, all reactions were conducted under dry nitrogen, with a nitrogen-filled dual manifold using standard Schlenk techniques. All solvents and reagents were obtained from commercial sources and used as received unless otherwise stated. *N*,*N*-Dimethylformamide was stirred over calcium hydride (20 h), distilled *in vacuo* and stored under nitrogen. Tetrahydrofuran, diethyl ether, toluene, and hexane were distilled from sodium and stored under nitrogen. Methylene

chloride was refluxed over calcium hydride, distilled and stored under nitrogen. 2,2'-Dibromobiphenyl⁵⁷ and *N*-octyl-9*H*-carbazole⁴⁵ were prepared according to literature procedures. For the synthesis of 2,2'-diiodobiphenyl, 5,5'-dibromo-2,2'-diiodobiphenyl, 3,6-dibromo-*N*-octyl-9*H*-carbazole, 3,6-dibromo-9,9dioctyl-9*H*-dibenzosilole, 9,9-dioctyl-3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9*H*-dibenzosilole (1), 2,7-bis(4,4,5,5tetramethyl-1,3,2-dioxaborolane-2-yl)-9,9-dioctyldibenzosilole (2), 4,4'-dibromo-2,2'-dinitrobiphenyl (3), 4,4'-dibromobiphenyl-2,2'-diamine (4), 2,7-dibromo-9,9-di-*n*-octyldibenzosilole (6) and a scheme for the synthetic route to dibenzosilole monomer 1, please refer to the ESI†. Polymer **P8** was further purified for OFET fabrication by use of a palladium scavenging agent (see ESI† for procedure).

Synthesis

4,4'-Dibromo-2,2'-diiodobiphenyl (5)²⁴. A 3-necked flask equipped with a low temperature thermometer was charged with 4,4'-dibromobiphenyl-2,2'-diamine (1.00 g, 2.6 mmol), aqueous HCl (10 mL, 32% w/w), H₂O (40 mL) and acetonitrile (40 mL). The mixture was warmed and stirred until the diamine was dissolved, then cooled to -10 °C, giving a light yellow precipitate. A solution of sodium nitrite (0.92 g, 13.4 mmol) in H₂O (5 mL) was cooled to 0 °C and added slowly to the reaction mixture, keeping the reaction temperature between -10 and -5 °C. The reaction was stirred at this temperature for one hour. A solution of KI (4.44 g, 26.7 mmol) in H₂O (10 mL) was cooled to 0 °C and added dropwise via cannula to the reaction mixture with vigorous stirring, whilst maintaining the reaction temperature between -15 °C and -10 °C. Once addition was complete, the reaction was warmed to room temperature and then heated to 80 °C for 20 h. The product was extracted with chloroform $(3 \times 100 \text{ mL})$ and the combined organic phases washed with aq. Na₂S₂O₃ (200 mL), H₂O (200 mL) and brine (200 mL), dried (MgSO₄) and evaporated to dryness. Purification by column chromatography on silica gel, using hexane as eluent, followed by recrystallisation from hexane yielded the title compound (0.88 g, 1.56 mmol, 58%) as colourless needles; mp 89-90 °C (from hexane, lit. mp 89 °C);²⁴ $R_{\rm F}$ (hexane) 0.32; $\delta_{\rm H}$ (400 MHz, CDCl₃) 7.03 (2H, d, J 8.1, ArH), 7.56 (2H, dd, J 8.1, 1.9, ArH), 8.09 (2H, d, J 1.9, ArH). The $\delta_{\rm H}$ data are in agreement with literature values.24

N,N-Bis(4-bromobenzene)-4-sec-butylaniline (7). An ovendried multi-necked round-bottomed flask was evacuated and filled with nitrogen. 4-sec-Butylaniline (2.46 mL, 16.1 mmol), 1-bromo-4-iodobenzene (10.00 g, 35.4 mmol), 1,10-phenanthroline monohydrate (127 mg, 0.6 mmol) and toluene (55 mL) were added under nitrogen. A Dean–Stark trap was fitted and the reaction mixture was stirred and degassed with nitrogen for 20 minutes. Copper(1) chloride (64 mg, 0.6 mmol) and ground, oven-dried potassium hydroxide (7.21 g, 128.5 mmol), were added under nitrogen and the mixture was stirred and degassed for a further 10 minutes, before being stirred for 20 h at reflux, under a nitrogen atmosphere. The reaction was allowed to cool to room temperature and distilled water (50 mL) was added. The aqueous layer was extracted with toluene (3×50 mL) and the combined organic layers were washed with 10% aqueous ammonia solution (100 mL), distilled water (100 mL), 10% aqueous thiosulfate solution (100 mL) and brine (100 mL). The solution was dried (MgSO₄) and the solvent was removed under vacuum to give a dark orange oil. Purification by column chromatography on silica, using petroleum ether 40-60% with 2% triethylamine, followed by recrystallisation from isopropyl alcohol afforded the title compound (2.41 g, 5.2 mmol, 33%) as white needles: mp 108–109 °C (from isopropyl alcohol): (found: C, 57.5; H, 4.6; N, 2.9. C₂₂H₂₁Br₂N requires: C, 57.5; H, 4.6; N, 3.05%); $R_{\rm F}$ (petrol-2%Et₃N) 0.52; $\delta_{\rm H}$ (400 MHz, CDCl₃) 0.83 (3H, t, J 7.5, CH₃), 1.21 (3H, d, J 7.0, CH₃), 1.53–1.63 (2H, m, CH₂), 2.59 (1H, tq, J7.0, 7.0, ArH), 6.92 (4H, d, J9.0, ArH), 6.98 (2H, d, J 8.5, ArH), 7.11 (2H, d, J 8.5, ArH), 7.33 (4H, d, J 9.0, ArH); δ_C (100 MHz, CDCl₃) 12.6, 22.1, 31.7, 41.7, 115.3, 125.5, 125.6, 128.7, 132.7, 144.4, 145.0, 147.4; m/z (ES) 458.0120 ([M + H^{+}_{2} . $C_{22}H_{22}^{79}Br_{2}N_{2}$ requires 458.0119), (ES⁺) 460 (100%), 245 (19), 153 (21).

N,*N*'-**Bis(3-bromobenzoyl)hydrazine** (8). A multi-necked round-bottomed flask was charged with 3-bromobenzoyl chloride (6.00 mL, 45.5 mmol) and *N*-methyl-2-pyrrolidinone (200 mL). The mixture was stirred and degassed with nitrogen for 20 minutes and then cooled to 0 °C before hydrazine mono-hydrate (4.42 mL, 91.1 mmol) was added dropwise under nitrogen. The reaction was stirred overnight at room temperature under a nitrogen atmosphere, then precipitated into distilled water (1.5 L). The precipitate was collected and washed thoroughly with EtOAc (500 mL) and petroleum ether 40–60 °C (50 mL), then dried under vacuum to afford the *title compound* (7.03 g, 17.8 mmol, 78%) as a fine white powder; mp >220 °C; $\delta_{\rm H}$ (400 MHz, DMSO) 7.51 (2H, dd, *J* 8.0, 8.0, Ar*H*), 7.82 (2H, d, *J* 8.0, Ar*H*), 7.92 (2H, d, *J* 8.0, Ar*H*), 8.09 (2H, s, Ar*H*), 10.67 (2H, s, N*H*).

2,5-Bis(3-bromophenyl)-1,3,4-oxadiazole (9). A multi-necked round-bottomed flask was evacuated and filled with nitrogen. N, N'-Bis(3-bromobenzoyl)hydrazine (1.20 g, 3.0 mmol) and phosphorous oxychloride (40 mL) were added under nitrogen and the mixture was stirred and degassed with nitrogen for 20 minutes. The reaction was then stirred at 130 °C, under nitrogen, for 7 hours. Once cooled to room temperature, the mixture was cautiously added to ice water. The mixture was maintained at 0 °C, whilst KOH pellets were added, until the solution was pH neutral. The aqueous layer was extracted with chloroform (3 \times 50 mL). The combined organic layers were washed with brine (200 mL), dried (MgSO₄) and dried in vacuo. Recrystallisation from ethanol afforded the *title compound* (1.01 g, 2.7 mmol, 88%) as fine colourless needles; mp 178-181 °C (from EtOH); (found: C, 44.2; H, 2.0; N, 7.3. C₁₄H₈Br₂N₂O requires: C, 44.2; H, 2.1; N, 7.4%); δ_H (400 MHz, CDCl₃) 7.41 (2H, dd, J 8.0, 8.0, ArH), 7.69 (2H, d, J 8.0, ArH), 8.08 (2H, d, J 8.0, ArH), 8.27 (2H, s, ArH); δ_C (100 MHz, CDCl₃) 88.8, 89.4, 89.4, 90.5, 90.7, 91.8, 99.0; *m/z* (ES) 378.9078 ($[M + H]^+$. $C_{14}H_9^{79}Br_2N_2O$ requires 378.9082), (ES⁺) 422 ([M + ACN + H]⁺, 80%), 381 (100), 342 (42).

1,2-Bis((3-bromophenyl)chloromethylene)hydrazine (10). A multi-necked round-bottomed flask was charged with N,N'-bis (3-bromobenzoyl)hydrazine (6.09 g, 15.4 mmol) and toluene (120 mL). The mixture was stirred and degassed with nitrogen for

30 minutes, whilst warming to 60 °C. Phosphorous pentachloride (7.05 g, 33.9 mmol) was added to reaction under nitrogen and the mixture was stirred at reflux for 20 h. On cooling to room temperature, the resultant yellow precipitate was collected and washed thoroughly with chloroform (100 mL) to afford the *title compound* (1.21 g, 2.8 mmol, 18%) as yellow crystals; mp 109–110 °C; (found: C, 38.6; H, 1.7. $C_{14}H_8Br_2Cl_2N_2$ requires C, 38.7; H, 1.9%); ν_{max}/cm^{-1} (neat solid) 681, 750, 790, 890, 932, 1212, 1404, 1468, 1557, 1599; $\delta_{\rm H}$ (400 MHz, DMSO) 7.57 (2H, dd, *J* 8.0, Ar*H*), 7.89 (2H, d, *J* 8.0, Ar*H*), 8.08 (2H, d, *J* 8.0, Ar*H*), 8.18 (2H, s, Ar*H*); $\delta_{\rm C}$ (100 MHz, *d*₆-DMSO) 122.9 (s), 128.1 (d), 131.0 (d), 132.0 (d), 135.0 (s), 136.1 (s), 159.1 (s); *m/z* (EI) 431.8426 (M⁺. $C_{14}H_8^{79}Br_2^{35}Cl_2N_2$ requires 431.8426), 436 (6%), 434 (7), 432 (3), 399 (7), 218 (12), 183 (100), 119 (13), 102 (32), 93 (16), 75 (19), 49 (23).

3,5-Bis(3-bromophenyl)-4-(4-(octyloxy)phenyl)-1,2,4-triazole (11). A multi-necked round-bottomed flask was charged with 4-octyloxyaniline (672 mg, 3.0 mmol) and 1,2-bis((3-bromophenyl)chloromethylene)hydrazine (1.20 g, 2.8 mmol), then evacuated and nitrogen-filled. N,N-Dimethylaniline (20 mL) was added under nitrogen and the mixture was stirred and degassed with nitrogen for 20 minutes, then stirred at 135 °C for 48 hours under a nitrogen atmosphere. The reaction mixture was allowed to cool to room temperature and precipitated into a beaker containing hydrochloric acid (2.0 mol dm⁻³, 100 mL), which was then stirred vigorously for 20 minutes. A light brown precipitate was collected and washed with distilled water. Recrystallisation from isopropyl alcohol afforded the *title compound* (1.05 g, 1.8 mmol, 66%) as colourless crystals; mp 96-97 °C (from isopropyl alcohol); (found: C, 57.5; H, 4.9; N, 7.1. C₂₈H₂₉Br₂N₃O requires C, 57.7; H, 5.0; N, 7.2%); $\delta_{\rm H}$ (400 MHz, CDCl₃) 0.87 (3H, t, J 6.5, CH₃), 1.22-1.50 (10H, m, CH₂) 1.74-1.84 (2H, m, CH₂), 3.98 (2H, t, J 6.5, CH₂), 6.93 (2H, d, J 9.0, ArH), 7.04 (2H, d, J 9.0, ArH), 7.14 (2H, dd, J 8.0, 8.0, ArH), 7.28 (2H, d, J 8.0, Ar*H*), 7.49 (2H, d, *J* 8.0, Ar*H*), 7.70 (2H, s, Ar*H*); δ_C (100 MHz, CDCl₃) 14.3, 22.8, 26.1, 29.2, 29.4, 29.5, 31.9, 68.7, 116.0, 122.7, 126.7, 127.1, 128.7, 128.9, 130.0, 131.9, 132.9, 153.9, 160.3; m/z (ES) 582.0746 ($[M + H]^+$. $C_{28}H_{30}^{79}Br_2N_3O$ requires 582.0756), (ES⁺) 647 ([M + ACN + Na]⁺, 12%), 584 (100).

General procedure for Suzuki polymerization-method A

A multi-neck round bottomed flask was charged with 3,6-bis (4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)-9,9-dioctyldibenzosilole (550 mg, 0.8 mmol), the chosen co-monomer (0.8 mmol), palladium(II)acetate (4 mg, 17 µmol) and toluene (20 mL). The mixture was stirred and degassed with nitrogen for 20 minutes. Tricyclohexylphosphonium tetrafluoroborate (25 mg, 69 µmol) and a degassed 20% aqueous solution of tetraethylammonium hydroxide (2 mL) were added under nitrogen. The reaction mixture was degassed for a further 10 minutes, then stirred at 110 °C for 48 hours, and finally allowed to cool to 25 °C. Bromobenzene (0.09 mL, 0.8 mmol), palladium(II)acetate (4 mg, 17 µmol) and tricyclohexylphosphonium tetrafluoroborate (25 mg, 69 µmol) were added under nitrogen. The mixture was stirred and degassed with nitrogen for 10 minutes, after which the reaction was stirred at 110 °C for 20 h and then allowed to cool to 25 °C. Phenylboronic acid (204 mg, 1.7 mmol),

palladium(II)acetate (4 mg, 17 μ mol) and tricyclohexylphosphonium tetrafluoroborate (25 mg, 69 μ mol) were added under nitrogen. The mixture was stirred and degassed with nitrogen for 10 minutes, after which the reaction was stirred at 110 °C for 20 h. The reaction was allowed to cool to room temperature. The organic layer was removed and filtered though a pad of silica. The solution was concentrated under vacuum, then added dropwise into a vigorously stirred flask of methanol (500 mL). The resulting precipitate was filtered and collected, then re-dissolved in methylene chloride and filtered through a plug of silica. The solution was again concentrated under vacuum and precipitated into a vigorously stirred flask of methanol (500 mL). The precipitate was filtered, washed with methanol and dried *in vacuo* to afford copolymer **P1–P4**.

General procedure for Suzuki polymerization-method B

A multi-neck round bottomed flask was charged with 2,7-bis(4,4,5,5tetramethyl-1,3,2-dioxaborolane-2-yl)-9,9-dioctyldibenzosilole (1.00 g, 1.5 mmol), the chosen co-monomer (1.5 mmol), palladium(II) acetate (7 mg, 31 µmol) and toluene (30 mL). The remaining procedure was as per method A, but using the following quantities: stage 1—tricyclohexylphosphonium tetrafluoroborate (46 mg, 125 µmol), tetraethylammonium hydroxide (20%, 3 mL); stage 2—bromobenzene (0.16 mL, 1.5 mmol), palladium(II) acetate (7 mg, 31 µmol), tricyclohexylphosphonium tetrafluoroborate (46 mg, 125 µmol); stage 3—phenylboronic acid (370 mg, 3.0 mmol), palladium(II)acetate (7 mg, 31 µmol), tricyclohexylphosphonium tetrafluoroborate (46 mg, 125 µmol). Precipitations: methanol (500 mL). Dried *in vacuo* to afford copolymer **P5–P8**.

α,ω-Diphenylpoly(N-octyl-9H-carbazole-3,6-diyl-9,9-dioctyl-9*H*-dibenzosilole-3,6-diyl) (P1). 3,6-Dibromo-N-octyl-9Hcarbazole (365 mg, 0.8 mmol) was used as the co-monomer, following general polymerisation method A, to afford the title compound (547 mg, 96%) as a yellow granulated, fibrous solid. (Found: C, 84.2; H, 9.5; N, 1.95. A repeat unit composition of C₄₈H₆₃NSi requires: C, 84.3; H, 9.6; N, 2.05%.) GPC in THF vs. narrow polystyrene standards revealed $M_{\rm w} = 6600$, $M_{\rm n} = 4800$, PDI = 1.38; $M_{\rm w}$ = 1600, $M_{\rm n}$ = 1500, PDI = 1.06; $\lambda_{\rm max}/{\rm nm}$ (CHCl₃ solution) 296; $\delta_{\rm H}$ (400 MHz, CDCl₃) 0.73–0.88 (br m, CH₂ and CH₃), 0.94–1.05 (br m, CH₂), 1.09–1.42 (br m, CH₂), 1.42-1.54 (br m, CH₂), 1.79-1.88 (br m, CH₂), 3.95-4.05 (br m, CH₂), 6.93-7.04 (m, ArH), 7.10-7.26 (br m, ArH), 7.27-7.54 (br m, ArH), 7.62–7.96 (br m, ArH), 8.04 (s, ArH); $\delta_{\rm C}$ (100 MHz, CDCl₃) 1.2, 12.5, 12.7, 14.3, 22.9, 24.2, 24.3, 25.1, 27.5, 29.4, 32.1, 33.7, 109.3, 119.4, 120.2, 123.7, 126.8, 133.9, 134.9, 136.2, 140.7, 141.9, 144.2, 144.3, 149.3.

α,ω-Diphenylpoly(9,9-dioctyl-9*H*-dibenzosilole-3,6-diyl-2,5-bis-(*m*-phenylene)-1,3,5-oxadiazole) (P2). 2,5-Bis(3-bromophenyl)-1,3,4-oxadiazole (317 mg, 0.8 mmol) was used as the co-monomer, following general polymerisation method A, to afford the *title compound* (464 mg, 89%) as an off-white powder. (Found: C, 80.35; H, 7.8; N, 4.4. A repeat unit composition of C₄₂H₅₀N₂OSi requires: C, 80.5; H, 8.0; N, 4.5%.) GPC assay in THF *vs.* narrow polystyrene standards revealed $M_w = 5600$, $M_n = 3300$, PDI = 1.70; λ_{max} /nm (CHCl₃ solution) 268; δ_H (400 MHz, CDCl₃) 0.51–1.43 (br m, CH₂ and CH₃), 1.72 (br s, CH₂), 7.31–7.93 (br m, Ar*H*), 8.02–8.21 (br m, Ar*H*), 8.21–8.51 (br m, Ar*H*); $\delta_{\rm C}$ (100 MHz, CDCl₃) 22.8, 23.3, 24.2, 29.3, 29.4, 32.1, 33.6, 120.1, 124.6, 125.8, 126.1, 126.9, 128.4, 129.0, 129.8, 134.1, 142.1, 149.0, 164.9.

α,ω-Diphenylpoly(4-(4-(octyloxy)phenyl)-3,5-bis(*m*-phenylene)-4*H*-1,2,4-triazole-9,9-dioctyl-9*H*-dibenzosilole-3,6-diyl) (P3). 4-(4-(Octyloxy)phenyl)-3,5-bis(3-bromophenyl)-4*H*-1,2,4-triazole (487 mg, 0.8 mmol) was used as the co-monomer, following general polymerisation method A, to afford the *title compound* (650 mg, 94%) as a light yellow fibrous powder. GPC assay in THF *vs*. narrow polystyrene standards revealed $M_w = 10500$, $M_n = 6900$, PDI = 1.52; $M_w = 1800$, $M_n = 1700$, PDI = 1.05; δ_H (400 MHz, CDCl₃) 0.74–1.01 (br m, CH₂ and CH₃), 1.01–1.45 (br m, CH₂), 1.58–1.81 (br m, CH₂), 3.71–3.98 (br m, CH₂), 6.71–7.02 (br m, Ar*H*), 7.02–7.81 (br m, Ar*H*), 8.03–8.62 (br m, Ar*H*); δ_C (100 MHz, CDCl₃) 12.6, 14.3, 22.8, 24.2, 25.1, 26.3, 29.3, 29.4, 32.0, 33.7, 68.7, 116.0, 119.9, 126.6, 127.2, 127.5, 127.8, 127.9, 128.1, 128.2, 129.0, 129.1, 129.3, 133.8, 137.7, 141.9, 142.2, 149.0.

α,ω-Diphenylpoly(bis(p-phenylene)-4-sec-butylphenylamine-9,9dioctyl-9H-dibenzosilole-3,6-diyl) (P4). Bis(4-bromophenyl)-4sec-butylphenylamine (383 mg, 0.8 mmol) was used as the co-monomer, following general polymerisation method A, to afford the title compound (541 mg, 92%) as a light yellow granulated solid. (Found: C, 84.9; H, 9.0; N, 1.9. A repeat unit composition of C₅₀H₆₁NSi requires: C, 85.05; H, 9.0; N, 2.0%.) GPC assay in THF vs. narrow polystyrene standards revealed $M_{\rm w} = 10\ 700,\ M_{\rm n} = 8000,\ {\rm PDI} = 1.34;\ M_{\rm w} = 2400,\ M_{\rm n} = 2100,$ PDI = 1.11; λ_{max}/nm (CHCl₃ solution) 353; δ_{H} (400 MHz, $CDCl_3$) 0.78–0.90 (m, CH_2 and CH_3), 0.92–1.01 (br m, CH_2), 1.11-1.33 (br m, CH₂), 1.33 (s, CH₃), 1.33-1.47 (br m, CH₂), 1.51-1.63 (br m, CH₂), 2.30-2.62 (br m, CH), 6.95-7.26 (m, ArH), 7.29–7.69 (m, ArH), 7.77–7.82 (m, ArH), 8.08 (br s, ArH); $\delta_{\rm C}$ (100 MHz, CDCl₃) 12.5, 12.7, 14.3, 22.0, 22.9, 24.3, 25.1, 29.4, 31.5, 32.1, 33.7, 41.3, 119.4, 123.9, 125.2, 125.3, 127.9, 128.2, 133.8, 135.0, 136.7, 142.8, 143.3, 144.9, 145.3, 147.5, 149.1.

α,ω-Diphenylpoly(*N*-octyl-9*H*-carbazole-3,6-diyl-9,9-dioctyl-9*H*-dibenzosilole-2,7-diyl) (P5). 3,6-Dibromo-*N*-octyl-9*H*-carbazole (365 mg, 0.8 mmol) was used as the co-monomer, following general polymerisation method B, to afford the *title compound* (994 mg, 96%) as a yellow granulated solid. GPC assay in THF *vs.* narrow polystyrene standards revealed $M_w = 5500$, $M_n =$ 3400, PDI = 1.61; λ_{max} /nm (CHCl₃ solution) 353; δ_H (400 MHz, CDCl₃) 0.75–0.90 (m, CH₂ and CH₃), 0.95–1.12 (br m, CH₂), 1.12–1.55 (br m, CH₂), 1.83–2.02 (br m, CH₂), 4.20–4.42 (br m, CH₂), 7.32–7.56 (m, ArH), 7.73–8.01 (m, ArH), 8.43–8.49 (m, ArH); δ_C (100 MHz, CDCl₃) 12.7, 14.3, 22.9, 24.2, 25.1, 25.9, 27.6, 29.4, 29.6, 32.1, 33.7, 119.1, 121.4, 123.8, 125.6, 127.9, 129.3, 131.5, 132.8, 135.0, 137.0, 138.9, 140.6.

α,ω-Diphenylpoly(9,9-dioctyl-9*H*-dibenzosilole-2,7-diyl-2,5-bis-(*m*-phenylene)-1,3,5-oxadiazole) (P6). 2,5-Bis(3-bromophenyl)-1,3,4-oxadiazole (577 mg, 1.5 mmol) was used as the co-monomer, following general polymerisation method B, to afford the *title compound* (863 mg, 88%) as a white fibrous solid. (Found: C, 80.4; H, 7.9; N, 4.4. Repeat unit composition of $C_{42}H_{50}N_2OSi$ requires: C, 80.5; H, 8.0; N, 4.5%.) GPC assay in THF vs. narrow polystyrene standards revealed $M_w = 4700$, $M_n = 4000$, PDI = 1.19; $M_w = 1800$, $M_n = 1700$, PDI = 1.04; $M_w = 700$, $M_n = 600$, $M_P = 1100$, PDI = 1.22; λ_{max}/mm (CHCl₃ solution) 320; δ_H (400 MHz, CDCl₃) 0.75–0.81 (m, CH₂ and CH₃), 0.81–1.37 (br m, CH₂), 1.37 (s, CH₃), 1.37–1.49 (br m, CH₂), 1.62 (br s, CH₂), 7.30–7.54 (m, ArH), 7.60–7.72 (br m, ArH), 7.72–8.02 (br m, ArH), 8.06–8.21 (br m, ArH), 8.31 (br s, ArH), 8.38–8.52 (br m, ArH); δ_C (100 MHz, CDCl₃) 12.3, 14.1, 22.6, 24.0, 24.9, 29.1, 29.2. 31.8, 33.4, 121.4, 121.6, 124.2, 124.5, 125.6, 125.6, 127.1, 127.3, 129.3, 129.6, 129.8, 130.5, 130.6, 132.0.

 α,ω -Diphenylpoly(4-(4-(octyloxy)phenyl)-3,5-bis(*m*-phenylene)-4*H*-1,2,4-triazole-9,9-dioctvl-9H-dibenzosilole-2,7-divl) (P7). 4-(4-(Octvloxy)phenyl)-3,5-bis(3-bromophenyl)-4H-1,2,4-triazole (886 mg, 1.5 mmol) was used as the co-monomer, following general polymerisation method B, to afford the *title compound* (1.14 g, 91%) as a light vellow fibrous solid. (Found: C, 80.9; H, 8.5; N, 4.9. A repeat unit composition of C₅₆H₆₉N₃OSi requires: C, 81.0; H, 8.6; N, 5.1%.) GPC assay in THF vs. narrow polystyrene standards revealed $M_{\rm w} = 12\ 200,\ M_{\rm n} = 6700,\ {\rm PDI} = 1.82;\ \lambda_{\rm max}/$ nm (CHCl₃ solution) 326; $\delta_{\rm H}$ (400 MHz, CDCl₃) 0.73–0.89 (m, CH₂ and CH₃), 1.10–1.39 (br m, CH₂), 1.41–1.52 (br m, CH₂), 1.79-1.84 (br m, CH₂), 3.96-4.09 (br m, CH₂), 6.95-7.04 (br m, ArH), 7.32-7.53 (br m, ArH), 7.64-7.90 (br m, ArH), 7.92 (br s, ArH); δ_C (100 MHz, CDCl₃) 12.5, 14.3, 22.8, 24.1, 26.3, 29.3, 29.4, 29.6, 32.0, 33.6, 116.0, 121.5, 127.5, 127.6, 128.0, 129.1, 129.2, 131.9, 138.9, 139.2, 141.7, 147.7, 155.0, 160.3.

α,ω-Diphenylpoly(bis(*p*-phenylene)-4-*sec*-butylphenylamine-9,9dioctyl-9*H*-dibenzosilole-2,7-diyl) (P8). Bis(4-bromophenyl)-4*sec*-butylphenylamine (697 mg, 1.5 mmol) was used as the co-monomer, following general polymerisation method B, to afford the *title compound* (0.98 g, 92%) as a bright yellow fibrous solid. GPC assay in THF *vs.* narrow polystyrene standards revealed $M_w = 11700$, $M_n = 5700$, PDI = 2.05; λ_{max}/nm (CHCl₃ solution) 390; δ_H (400 MHz, CDCl₃) 0.78–0.90 (m, CH₂ and CH₃), 0.93–1.03 (br m, CH₂), 1.13–1.47 (br m, CH₂), 1.54–1.64 (m, CH₂), 2.52–2.63 (m, CH), 6.95–7.26 (m, ArH), 7.51–7.68 (m, ArH), 7.78–7.92 (m, ArH), 8.04 (s, ArH); δ_C (100 MHz, CDCl₃) 1.2, 12.6, 14.3, 22.0, 22.9, 24.2, 25.1, 29.3, 29.5, 31.5, 32.1, 33.6, 41.3, 121.4, 124.0, 125.1, 127.8, 127.9, 128.1, 128.2, 128.7, 131.6, 132.3, 135.3, 138.9, 139.4, 147.1, 147.3.

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