# Poly(dibenzosilole)s

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**Abstract** Poly(dibenzosilole)s are an emerging class of polymers with similar optoelectronic properties to polyfluorenes. With increased stability towards oxidation, several poly(dibenzosilole)-based devices, such as light emitting diodes, have shown improved performance over their polyfluorene counterparts. As a consequence of reduced conjugation in the polymer chain, some poly(dibenzosilole)s have high triplet excited state energies, which make them suitable hosts for blue triplet emitters in electrophosphorescent devices.

**Keywords** Conjugated polymer · Dibenzosilole · Light emitting diode ·
Organic electronic materials

**Abbreviations**

| | |
|---|---|
| CIE | Commission internationale de l'éclairage |
| CV | Cyclic voltammetry |
| EL | Electroluminescence |
| GPC | Gel permeation chromatography |
| HOMO | Highest occupied molecular orbital |
| ITO | Indium tin oxide |
| LUMO | Lowest unoccupied molecular orbital |
| OFET | Organic field effect transistor |
| OLED | Organic light emitting diode |
| OSC | Organic solar cell |
| PCBM | [6,6]-Phenyl-$C_{61}$ butyric acid methyl ester |
| PEDOT:PSS | Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) |
| PF8 | Poly(9,9-dioctylfluorene) |
| PL | Photoluminescence |

# 1
# Introduction

The area of conjugated polymers has grown into a major field of research since the discovery of highly conductive polyacetylenes in 1977 [1, 2]. Other properties of conjugated polymers have drawn increasing attention including electroluminescence for organic light emitting diodes (OLED) [3], high charge carrier mobility for organic field effect transistors (OFET) [4], tunable electronic properties for application in organic solar cells (OSC) [5] and response to physical and chemical stimuli for sensory applications [6]. Over the past decade, significant efforts have been devoted to developing conjugated polymers for application in multicolour OLED displays [7–9]. Polyfluorene and derivatives have emerged as the dominant class of polymers for commercial application [10–13]. They have been shown to exhibit high luminescence quantum efficiencies, thermal stability and good solubility. However, blue polyfluorene-based OLEDs suffer from poor spectral stability, which is characterized by the emergence of a broad and featureless low energy green emission band in the luminescence spectrum. This spectral instability has been linked to excimer formation as well as keto defects in the polymer chain [14–16]. Excimer formation can be suppressed by the introduction of bulky substituents to the polymer chain to increase interchain distances. Keto defects can be eliminated by careful synthetic preparation [17] or by replacing the vulnerable C-9 bridgehead atom with a heteroatom that is not easily oxidised. Although nitrogen [18–20], phosphorus [21] and sulfur [22] analogues of polyfluorene have all been prepared and some have shown stable blue emission, their low solubility in various organic solvents has limited processibility. Figure 1 shows the structures of some fluorene analogues.

Silicon and germanium have emerged as promising candidates as polyfluorene analogues (Fig. 1) [23]. They belong to the same periodic group as car-
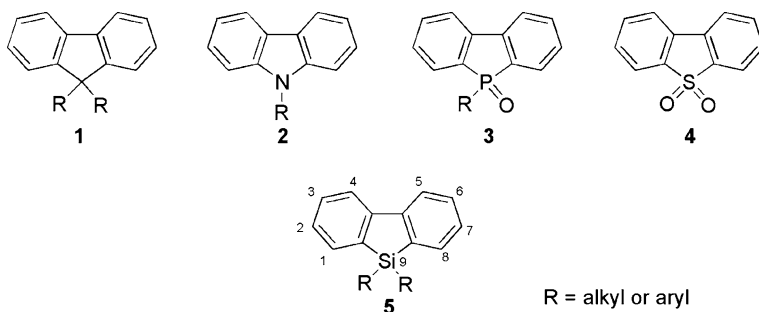


**Fig. 1** Structural illustrations of fluorene **1**, carbazole **2**, dibenzophosphole oxide **3**, dibenzothiophene dioxide **4** and dibenzosilole **5** with ring numbering

bon, and have been extensively exploited in both organic and inorganic semi-conductors. Aside from the potential of eliminating low wavelength emission, their solubility and processibility are close to that of polyfluorenes A further attraction of such a polymer is the expected enhancement of electron affinity owing to the $\sigma^*$–$\pi^*$ conjugation, as observed in analogous molecular and polymeric siloles [24, 25]. The silicon analogue, poly(dibenzosilole), has attracted some attention in recent years as a polymer for blue OLEDs as well as in other organic electronic applications. This article will survey the current literature concerning poly(dibenzosilole)s. A more general review of silicon-containing polymers has recently appeared [26].

# 2
# Synthesis

Early examples of the dibenzosilole unit were reported by Gilman and Gor-sich in the 1950s [27–29]. The silicon analogue of 9,9-diphenylfluorene, 9,9-diphenyldibenzosilole, was obtained from the dilithiation of 2,2′-dibromo-biphenyl followed by treatment with diphenyldichlorosilane [29]. 9,9-Di-methyldibenzosilole has also been prepared by reacting phenyl radicals with diphenyldimethylsilane [30]. The first report of incorporating the dibenzo-silole unit in a polymer came in 1983 [31], but it was not until the 1990s that several patents covering dibenzosiloles were filed. Their applications include electroluminescence [32, 33], semiconducting material for dye sensi-tized solar cells [34] and photoresist applications [35]. However, full synthetic procedures for dibenzosilole monomers and their corresponding polymers were only reported in recent years. The synthesis and electroluminescent properties of poly(2,7-dibenzosilole) **12** were reported by Holmes and co-workers in 2005 [23]. 2,7-Dibromodibenzosilole **10** was obtained from the selective lithiation of 4,4′-dibromo-2,2′-diiodobiphenyl **9** and treatment with dichlorodihexylsilane (Scheme 1). 4,4′-Dibromo-2,2′-diiodobiphenyl **9** was synthesised from 2,5-dibromonitrobenzene **1** following an Ullmann coupling, reduction, diazotisation/iodination sequence. The boronic acid pinacol ester **11** was obtained from 2,7-dibromodibenzosilole by lithiation and treatment with 2-isopropoxy-4,4′,5,5′-tetramethyl-1,3,2-dioxaboralane. Suzuki cross-coupling polymerisation of the dibromo and diboronic acid pinacol ester derivatives gave poly(2,7-dibenzosilole) in excellent yield. Huang and cowor-kers have also synthesised copolymers containing the dibenzosilole unit from 2,7-dibromodibenzosilole monomer **16** [36]. This monomer was obtained from *o*-dianisidine **13** by diazotization, iodination followed by lithiation and quenching with dichlorodimethylsilane (Scheme 2). Suzuki coupling has also been used to make copolymers of 2,7-dibenzosilole unit with thiophene [37] and dithienyl-benzothiadiazole [38] with application in thin-film transistors and polymer solar cells respectively.
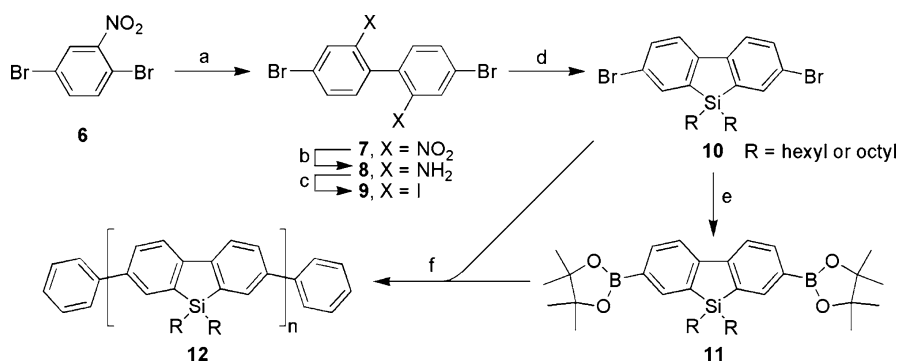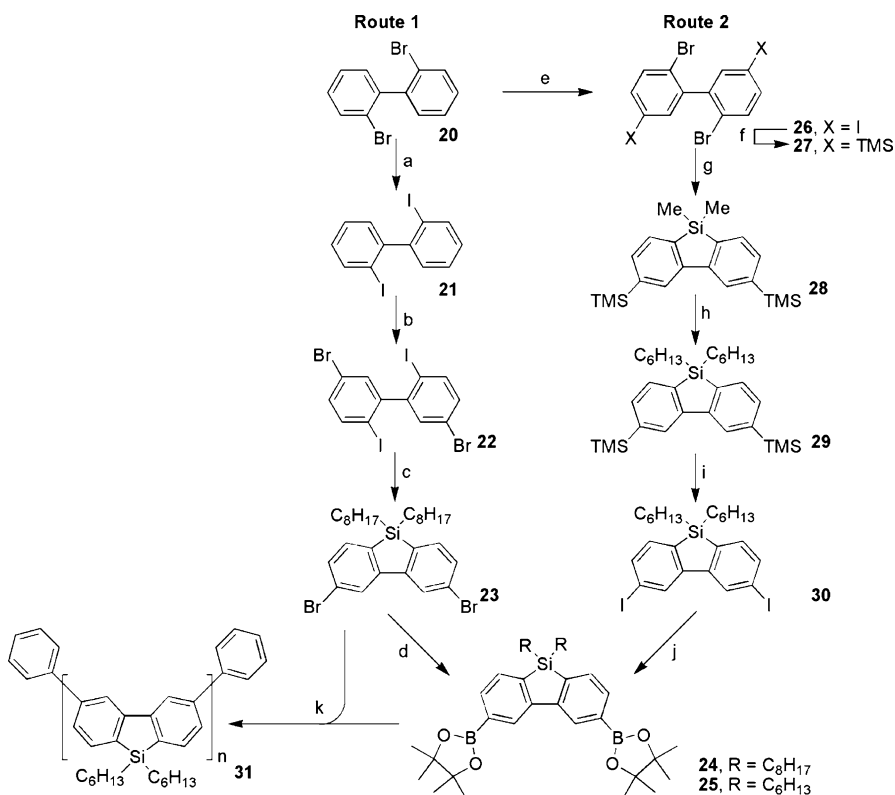
**Scheme 1** Synthesis of poly(2,7-dibenzosilole) [23]. Reagents and conditions: (a) Cu, DMF, 125 °C, 88%; (b) Sn, HCl, EtOH, 110 °C (bath temp), 72%; (c) nitrosylsulfuric acid, concentrated $H_2SO_4$, 0 °C, then aq. KI, – 10 to 50 °C, 30%; (d) *t*-BuLi (4 equiv), THF, – 90 to – 78 °C, then dichlorodihexylsilane or dichlorodioctylsilane, 25 °C, 52%; (e) *t*-BuLi, diethyl ether, – 78 °C, then 2-isopropoxy-4,4′,5,5′-tetramethyl-1,3,2-dioxaboralane, 25 °C, 86%
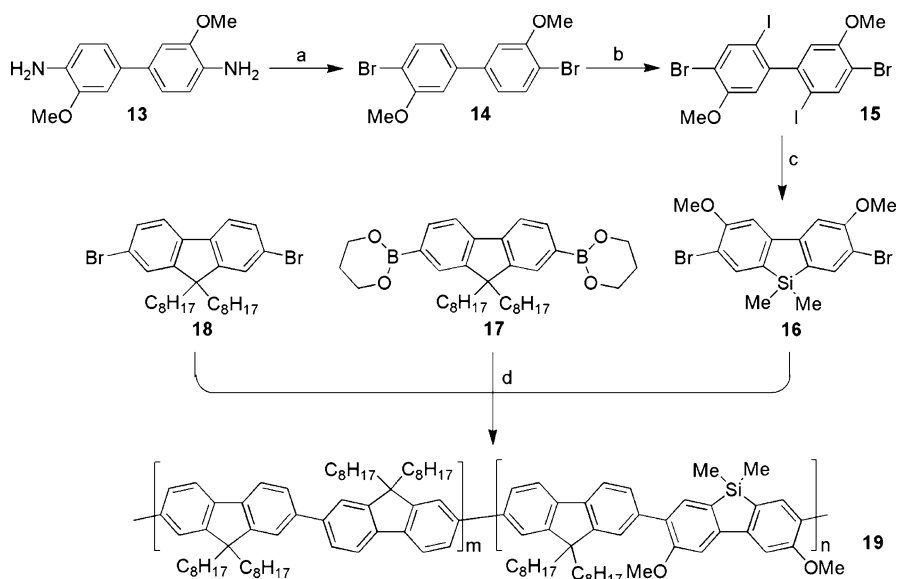


**Scheme 2** Synthesis of poly(2,7-fluorene-co-2,7-dibenzosilole) [36]. Reagents and conditions: (a) $NaNO_2$, CuBr, HBr (40%), 0 °C; (b) $I_2$, $KIO_3$, $H_2SO_4$, AcOH, 90 °C; (c) 2 equiv *n*-BuLi, 2 equiv dichlorodimethylsilane, THF, – 100 °C; (d) Pd(PPh₃)₄ (2 mol %), toluene/2 M $K_2CO_3$, 90 °C

3,6-Dibenzosilole monomers have also been reported in the literature [39–41]. Two routes were reported by Holmes and coworkers starting from 2,2′-dibromobiphenyl (Scheme 3) [41]. In Route 1, 2,2′-dibromobiphenyl was converted to 2,2′-diiodobiphenyl by treatment with $n$-BuLi followed by iodine. Regioselective bromination followed by selective silacyclisation afforded dibenzosilole **23**. Double lithiation of **23** and boronation gave dibenzosilole boron acid ester **24**. Cao and coworkers obtained the 3,6-dibenzosilole monomers through diamine intermediates using the diazoti-



**Scheme 3** Synthesis of poly(3,6-dibenzosilole) reported by Holmes and coworkers [41]. Reagents and conditions: (a) $n$-BuLi, THF, – 78 to 25 °C, 24 h, then $I_2$ in $Et_2O$, 0 °C, 2 h, 85%; (b) $Br_2$, Fe, $CHCl_3$, 50 °C, 24 h, 50%; (c) $t$-BuLi (4.2 equiv), THF, – 90 °C, $(C_8H_{17})_2SiCl_2$, 25 °C, 64%; (d) $t$-BuLi, THF, – 78 °C, then 2-isopropoxy-4,4′,5,5′-tetramethyl-1,3,2-dioxaboralane, 25 °C, 75%; (e) $I_2$, $NaIO_4$, conc. $H_2SO_4$, AcOH, $Ac_2O$, 24 h, 40%; (f) $n$-BuLi, – 78 °C, 24 h, then TMSCl, – 78 to 25 °C, 24 h, 84%; (g) $t$-BuLi, – 78 to 25 °C, 24 h, $SiMe_2Cl_2$, – 78 to 25 °C, 24 h, 81%; (h) $n$-HexLi, – 78 °C, 15 min, 95%; (i) ICl, $CH_2Cl_2$, 25 °C, 1 h, 90%; (j) $t$-BuLi, THF, – 78 °C, then 2-isopropoxy-4,4′,5,5′-tetramethyl-1,3,2-dioxaboralane, – 78 to 25 °C, 24 h, 42%; (k) **23**, **24**, $Pd(OAc)_2$, tricyclohexylphosphine, $Et_4NOH$, toluene, 90 °C, then $PhB(OH)_2$, 2 h, then PhBr, 2 h, 93%
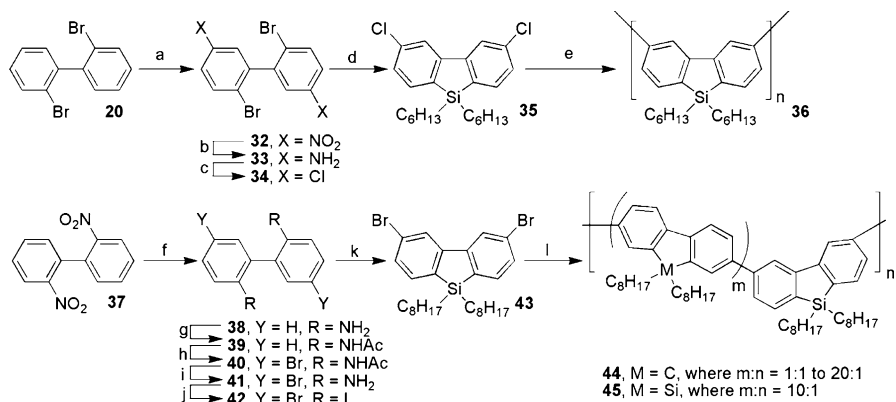
**Scheme 4** Synthesis of poly(3,6-dibenzosilole) reported by Cao and coworkers [39, 40, 42]. Reagents and conditions: (a) $HNO_3/H_2SO_4$; (b) HCl/Fe, EtOH; (c) $NaNO_2$/HCl, CuCl; (d) BuLi, – 65 °C, $(C_6H_{13})_2SiCl_2$; (e) $NiCl_2$, triphenylphosphine, 2,2′-bipyridine, Zinc, DMF; (f) Fe, HCl; (g) acetic anhydride, $Na_2CO_3$; (h) NBS, DMF; (i) HCl, EtOH; (j) $NaNO_2$/HCl, KI; (k) *n*-BuLi, – 65 °C, $(C_8H_{17})_2SiCl_2$; (l) $Pd(OAc)_2/Et_4NOH$, tricyclohexylphosphine, **17** and **18** or **10** and **11**

zation strategy (Scheme 4) [39, 40]. Using these monomers, homopolymers **31** and **36**, as well as various high energy copolymers [39, 42] **44** and **45**, have been synthesised by Yamamoto [40] and Suzuki [41] coupling methods (Schemes 3 and 4).

In a recent communication, an asymmetric dibenzosilole moiety was reported [43]. Using an iridium-catalysed [2 + 2 + 2] cycloaddition of silicon-bridged diynes and alkynes, various asymmetric dibenzosilole units were obtained in yields of up to 93% (Scheme 5). These novel dibenzosilole compounds can potentially lead to AB monomers for polymerisation. Ladder-
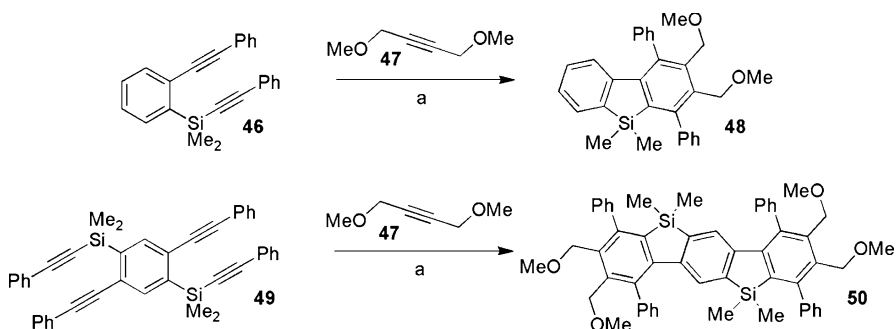


**Scheme 5** Synthesis of dibenzosilole using iridium-catalyzed [2 + 2 + 2] cycloaddition [43]. Reagents and conditions: (a) $[IrCl(COD)]_2$ 2.5 mol %, $PPh_3$ 10 mol %, $Bu_2O$, 110 °C, 24 h

type dibenzosilole compounds, such as **50**, were also synthesised using the same method opening an opportunity for the synthesis of dibenzosilole-based rigid planar polymers (Scheme 5).

Non-conjugatively linked 9,9'-dibenzosilole polymers have also been reported [44, 45]. In an early paper, a dehydrogenation catalyst, bis(1,5-cyclo-octadiene)palladium, was used in the synthesis of poly(9,9-dibenzosilole) **52** (Scheme 6) [45]. Recently, poly(dibenzosilole-vinylene)s **54** were obtained from the platinum-catalysed hydrosilylation of 9,9-dihydrodibenzosilole **51** with 9,9-diethynyldibenzosilole **53** (Scheme 6) [44].
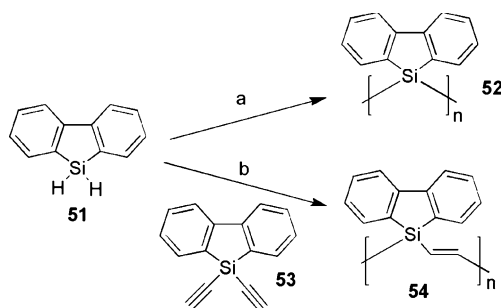


**Scheme 6** Synthesis of poly(dibenzosilole-vinylene) [44] and poly(9,9-dibenzosilole) [45]. Reagents and conditions: (a) Pd(COD)$_2$, toluene, 80 °C, 24 h; (b) H$_2$PtCl$_6$, toluene, 70 °C, 24 h

# 3
# Chemical and Physical Properties

The optical properties of poly(9,9-dihexyl-2,7-dibenzosilole) **12** are remarkably similar to those of poly(9,9-dioctyl-2,7-fluorene) (PF8) [23]. The absorption maximum in the UV-vis spectrum of a thin film of 7 ($\lambda_{max}$ = 390 nm) is comparable with that of PF8 ($\lambda_{max}$ = 389 nm), and the optical band gaps, determined from the $\lambda_{0-0}$ band edges, are 293 eV for both polymers. The photoluminescence (PL) emission maximum (excitation at 325 nm) of a film of polymer **12** at 425 nm and its two vibronic sidebands at 449 and 482 (CIE coordinates $x$ = 0.15, $y$ = 0.11, PL efficiency = 62%) are all within 3 nm of the corresponding bands for PF8 (PL efficiency = 60%). However polymer **12**, with a glass transition temperature of 149 °C, is thermally more stable than PF8. Moreover, on annealing at 250 °C for 16 h under air and ambient light, the PL spectrum of polymer **12** remains unchanged whereas a broad green band centered at 535 nm emerged in the PL spectrum of PF8 after annealing (Fig. 2). The HOMO and LUMO levels of polymer **12** in thin films were determined by cyclic voltammetry (CV) to be – 5.77 and – 2.18 eV respec-
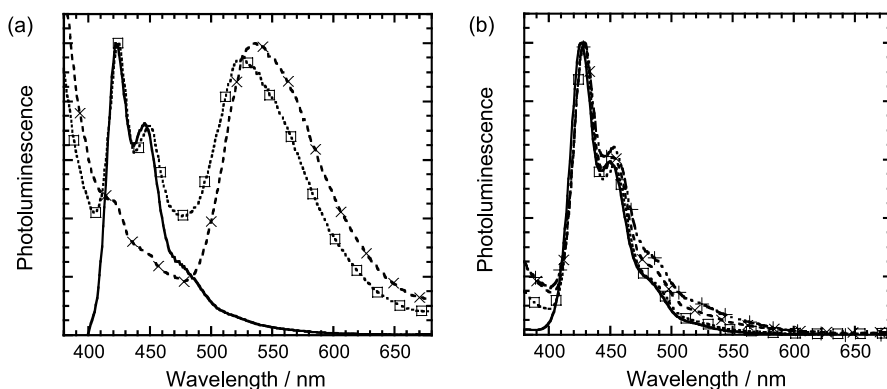
**Fig. 2** Normalized photoluminescence spectra of thin films of polymers before annealing (○), and after annealing for 2 h at 150 °C (□), 4 h at 200 °C (×) and 24 h at 250 °C (+) under ambient light and atmosphere. **a** Polyfluorene PF8. **b** Poly(dibenzosilole) **12**

tively, which is about 0.1 eV lower than that of PF8 measured under the same conditions (Fig. 3) [23].

The PL spectrum of a thin film of poly(3,6-dibenzosilole) **31** at 77 K exhibited a 0–0 transition at 3.5 eV and a second maximum at 3.3 eV (excitation at 4.4 eV) [41]. The phosphorescence emission spectrum at 77 K consists of a broad band exhibiting vibronic structure (excitation at 3.9 eV). The polymer triplet energy level was taken to be the onset of triplet emission at 2.55 eV. This is considerably higher than the triplet energy of commonly used polyfluorenes (2.1 eV) [10, 46] making it a host for phosphorescent emitters without the risk of energy back-transfer onto the polymer.
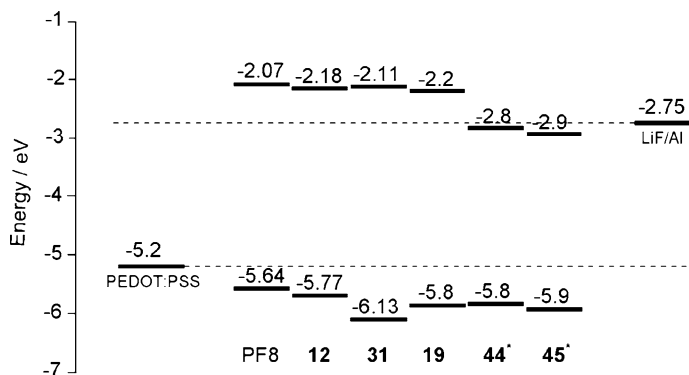


**Fig. 3** A schematic diagram showing the HOMO and LUMO energy levels of various polymers of fluorene and dibenzosilole, as well as the energy levels of PEDOT:PSS and LiF/Al electrode. * The energy levels of polymers **44** and **45** are reported in comparison to differing HOMO and LUMO levels for PF8 at – 5.80 and – 2.87 respectively [39, 42]

Cao and coworkers reported almost identical figures for the same polymer with no endcaps **36** [40]. Thermal gravimetric analysis showed excellent thermal stability with decomposition temperature at 442 °C, while its glass transition temperature is similar to that of poly(9,9-dioctyl-2,7-fluorene) at 83 °C. It is worth noting that molecular weights of poly(3,6-dibenzosilole)s (23 000/11 000 $M_w/M_n$ and polydispersity of 2.1) [41] are much lower than that of poly(2,7-dibenzosilole)s (425 000/109 000 $M_w/M_n$ and polydispersity of 3.9) [23], measured using gel permeation chromatography (GPC), referenced against polystyrene standards. This is also observed in polyfluorenes and other bridged phenylene polymers in general. From CV measurements, the HOMO level was determined to be – 5.65 eV for polymer **31** [41] (Fig. 3) and – 6.1 eV for polymer **36** [40], while the LUMO energy level was estimated to be approximately – 2.1 eV for both polymers.

The properties of copolymers involving dibenzosilole monomers have been reported by several groups [23, 36–39, 42]. Huang and coworkers studied a series of poly(9,9-dioctyl-2,7-fluorene-co-2,7-dibenzosilole)s **19** with varying ratios of fluorene and dibenzosilole units [36]. With increasing ratio of dibenzosilole to fluorene, the absorption ($\lambda_{max} \sim 380$ nm) and emission spectra ($\sim 420$ nm) are slightly blue shifted. This change in absorption and emission spectra was attributed to the shortening of average conjugation length in the copolymer with increasing incorporation of the dibenzosilole unit. Similar to PF8, a green emission at around 530 nm was observed for the copolymers after annealing in air at 200 °C. The HOMO and LUMO energy levels of this series of copolymers are very similar to that of PF8 at – 5.8 and – 2.2 eV respectively (Fig. 3). The increased proportion of the dibenzosilole unit in the polymer slightly raised the HOMO and lowered the LUMO giving a smaller band gap [36]. The reported LUMO of copolymers **44** and **45** is significantly lower than that of other dibenzosilole polymers shown in Fig. 3. This is most likely an artifact of the method of energy level measurement used by the investigators as the LUMO and HOMO levels of poly(9,9-dioctylfluorene) are reported to be – 2.87 and – 5.80, respectively [39, 42]. Other copolymers designed for specific device applications will be discussed in the next section [37, 38].

# 4
# Organic Electronic Devices

Although polyfluorene has been a popular active layer material for OLEDs, it suffers from oxidative degradation characterized by the emergence of a green emission band. Poly(2,7-dibenzosilole), with its higher thermal stability and resistance to oxidation, is a potential alternative to polyfluorene [23]. OLEDs fabricated from poly(2,7-dibenzosilole), with a configuration of ITO/PEDOT:PSS/polymer(65 nm)/Ba/Al, showed emission maxima

at 431 and 451 nm and operated more efficiently than a device fabricated from PF8.

With its high triplet energy, poly(3,6-dibenzosilole) is a suitable host for triplet emitters. Electrophosphorescent devices containing poly(3,6-dibenzosilole) as polymer host and iridium complexes as triplet emitters have been reported [41, 47]. In one study, a green phosphorescent dopant, *fac*-tris[2-(2-pyridyl-$\kappa N$)-5-methylphenyl]iridium(III), was blended into a toluene solution of polymer **31** (8 wt. %) and deposited in a device with configuration ITO/PEDOT:PSS/polymer blend/LiF/Al [41]. The electroluminescence (EL) spectrum of this device showed an emission maximum at around 540 nm. No emission was detected from the polymer indicating complete energy transfer from the polymer host to the green dopant. Cao and coworkers reported a similar system with a blue phosphorescent iridium dopant [47]. In comparison with the use of polyvinylcarbazole (PVK) as the polymer host, poly(3,6-dibenzosilole) **36** devices gave much higher external quantum and luminous efficiencies. Cao and coworkers also observed an interesting phenomenon whereby the PL spectrum of the polymer/iridium blend showed emission from the polymer only while the EL spectrum showed emission from the iridium complex alone (Fig. 4) [47]. This difference in PL and EL spectra was attributed to a Förster transfer mechanism in the PL process in contrast to a charge trapping mechanism in the EL process. The
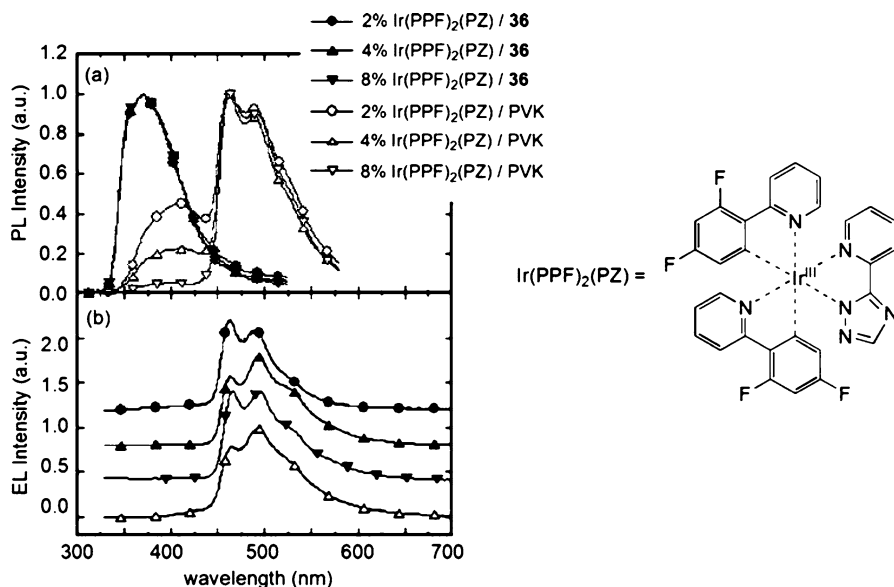


**Fig. 4 a** PL spectra of the iridium complex with different concentration doped into **36** and PVK, respectively. **b** EL spectra of devices Ir complex doped into **36** and PVK. Reprint with permission from [47]. © 2006, American Institute of Physics
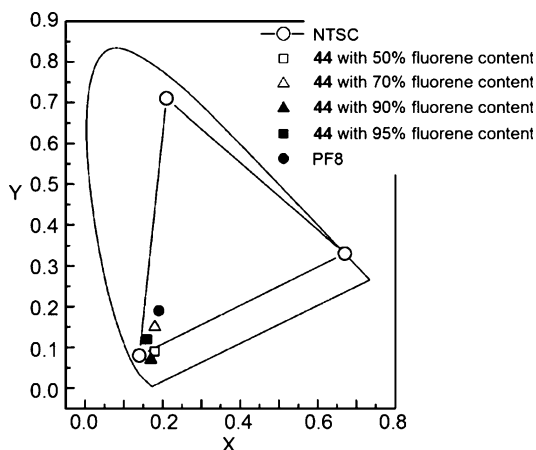
**Fig. 5** CIE coordinates of OLED devices fabricated from copolymers **31** [39]. Reproduced by permission of the Royal Society of Chemistry

authors speculate that the triplet energy level of poly(3,6-dibenzosilole) **36** is lower than that of the iridium complex, allowing the back transfer of energy in PL. Using PVK as the polymer host, which has no low energy triplet states, both EL and PL spectra showed emission from the iridium complex only [48].

Polymer LEDs with copolymers containing dibenzosiloles have been reported in the literature [39, 42]. By varying the 3,6-dibenzosilole content in a fluorene-based polymer, superior colour purity and optimum external quantum and luminous efficiencies were obtained (Fig. 5) [39]. Compared to polyfluorene, these copolymers are also stable to thermal annealing. Similar results were reported for a 2,7-dibenzosilole-*co*-3,6-dibenzosilole polymer [42].

A copolymer of 2,7-dibenzosilole and dithienylbenzothiadiazole **55** has been employed as the hole transport material in organic solar cells [38]. In CV measurements, the HOMO and LUMO energy of the polymer were determined to be 5.70 and 3.81 eV, respectively, making it a suitable partner for the commonly used electron transport material, [6,6]-phenyl-$C_{61}$ butyric acid methyl ester (PCBM), in bulk heterojunction solar cells. Devices, with structure ITO/PEDOT:PSS/polymer-PCBM 1 : 4/Al, tested under AM 1.5 G illumination showed a power conversion efficiency of 16% with open circuit voltage of 0.97 V and a fill factor of 55% (Fig. 6). These figures are comparable to other polymer/PCBM bulk heterojunction solar cells reported to date. A very similar polymer to **55** has been reported recently in a red light-emitting device [49]. Along with a green light-emitting poly(2,7-dibenzosilole-*co*-benzothiadiazole), it was found that their device efficiencies are higher than that of the fluorene analogues.

Copolymers of dibenzosilole and thiophene have also been used as semiconductors for OFET [37]. Carrier mobilities approaching 0.1 cm$^2$/Vs have
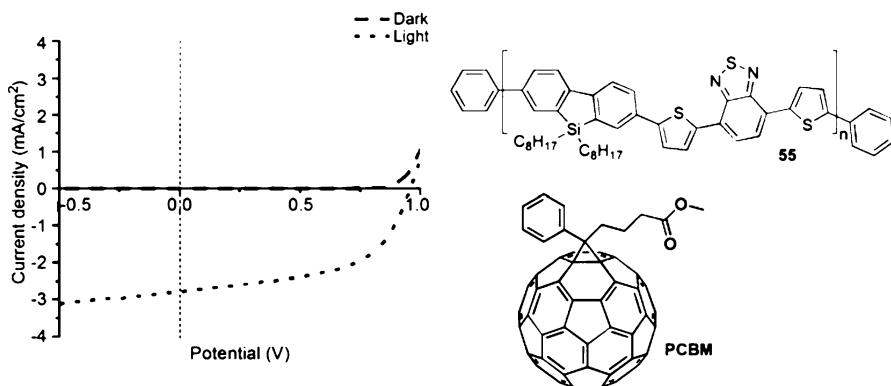
**Fig. 6** Current density-potential characteristic of the PCBM/copolymer **55** 4 : 1 bulk heterojunction organic solar cell under illumination with AM 1.5 G solar simulated light (*dotted line*) and in the dark (*dashed line*) [38]. © Wiley. Reproduced with permission

been measured in these OFETs. In a different area of application for dibenzosilole polymers, a non-conjugated 9,9-dibenzosilole polymer was used in the detection of various explosive chemicals [44]. Many high explosives contain multiple nitro substituents making them great electron acceptors. Explosive detection was achieved by fluorescence quenching of the polymer by electron transfer to the explosive compound. A $0.3\,\mathrm{ng/cm^2}$ solid state detection limit was achieved for TNT with the 9,9-dibenzosilole polymer.

# 5
# Conclusion

Poly(dibenzosilole)s are a relatively new class of compounds for the area of organic electronic materials. Poly(dibenzosilole)s are not easily oxidised and have advantages of solubility and processibility over other polyfluorene analogues, such as carbazoles, dibenzophosphole oxides and dibenzothiophene dioxides. Several groups have already incorporated poly(dibenzosilole)s in the latest organic electronic devices such as OLEDs, OFETs and OSCs and have found improved performance over similar polyfluorene-based devices. With continual advancement in their synthesis, dibenzosilole-based polymers are set to match the popularity of polyfluorenes in organic electronic materials.

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