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Preparation and properties of alternating 2,7-linked carbazole copolymers with phenylene units with varying number of fluorine substituents

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Abstract New alternating copolymers comprising 2,7-linked-3,6-dimethyl-9-(2-hexyldecy)-*9H*-carbazole and 1, 4-phenylene units (**P1**), 2,5-difluoro-1,4-phenylene units (**P2**), and 2,3,5,6-tetrafluoro-1,4-phenylene units (**P3**) have been prepared using Suzuki cross-coupling conditions. The polymers were characterized by NMR spectroscopy, UV–vis absorption spectroscopy, fluorescence spectroscopy, and their weight-average molecular weights were estimated using gel permeation chromatography. The polymers are thermally stable up to 420 °C and display wide band gaps ranging from 3.16 to 3.2 eV. The polymers are electrolytically stable and emit around 400 nm. A discussion on the effect of the varying degree of fluorine substitution of the phenylene repeat units in polymers **P1**–**P3** on their physical properties is presented.

Introduction

Recently, much effort has been devoted to develop wide band gap conjugated polymers for application in light emitting diodes. These materials are used either as blue emitters in electroluminescent devices or hosts to lower band gap fluorophores [1] and phosphorescent dyes in an effort to enable the use of both singlet and triplet excitons in the radiative decay process [2–7]. A great deal of attention has focused on developing derivatives of poly(*p*-phenylene)s and poly(9,9′-dialkylfluorene)s as wide band gap materials that could be used in these applications [8, 9]. The stability of blue light emission from devices made from this class of materials is often compromised by either excimer emission arising from aggregates in films or formation of fluorenone repeat units as a result of oxidation [10, 11] or a combination of both of these [12].

We have been interested in the development of alternative wide band gap conjugated polymers. We and others have shown recently that poly(9-alkyl-*9H*-carbazole-2,7-diyl)s [13–15] offer many advantageous properties. These polymers are highly fluorescent and emit in the blue part of the electromagnetic spectrum, however, cyclic voltammetric studies on this class of polymers have revealed that they do oxidize irreversibly under electrolytic conditions. We have also shown [16] that upon methyl-substitution of the 3,6-positions of the carbazole repeat units the polymers obtained are much more stable to oxidation under electrolytic conditions. Introduction of fluorine substituents on the backbone of poly(*p*-phenylenevinylene) polymers was shown to provide the possibility to alter the energy levels of these materials without imparting significant changes in the magnitude of their charge carrier mobilities and their optical properties [17]. It was also shown in recent studies that introduction of fluorinated phenylene repeat units as part of the chain in different polymers imparted the resulting materials with enhanced stability as well as different physical properties in the design of materials for electronic devices such as field effect transistors [18] and light emitting diodes [19, 20].

In this study, we present our results on the preparation and characterization of a range of blue emitting carbazole main chain copolymers comprising 2,7-linked-3,6-dimethyl-9-alkyl-*9H*-carbazole units and *p*-phenylene units with different number of fluorine substituents. The optical and electrochemical properties of the different copolymers will also be discussed.

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Experimental section

Materials

2,7-Dibromo-3,6-dimethyl-9-(2-hexyldecyl)-*9H*-carbazole **2** and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,6-dimethyl-9-(2-hexyldecyl)-9*H*-carbazole **3** were made according to literature procedures [16]. 1,4-Phenylenebisboronic acid, 1,4-dibromo-2,5-difluoro-benzene **4a** and 1,4-dibromo-2,3,5,6-tetrafluoro-benzene **4b** were obtained commercially. Toluene was dried and distilled over sodium under an inert argon atmosphere. Acetonitrile (HPLC grade) was dried and distilled over phosphorus pentoxide under an inert argon atmosphere, then stored over molecular sieves 3 Å.

Measurements

NMR spectra were recorded on Bruker 250 MHz, AMX400 400 MHz, or DRX500 500 MHz NMR spectrometers at 22 °C in chloroform-d_1 solutions with TMS as the internal standard. IR absorption spectra were recorded on the Nicolet Model 205 FT-IR Spectrometer. Liquid samples were analyzed using NaCl-plate method, and solid samples were analyzed using the Diamond ATR attachment method. GPC curves were recorded on the equipment consisting of Waters Model 515 HPLC Pump, GILSON Model 234 Autoinjector, MILLIPORE Waters Lambda-Max Model 481 LC Spectrometer, Erma ERC-7512 RI Detector, PLgel 5 m 500A Column, and PLgel 10 m MIXED-B Column using THF as the eluent at a rate of 1 cm^3 min^{-1}. Polymer solutions in THF (2.5 mg cm^{-3}) were used as samples for GPC analysis. The GPC curves were obtained by the RI-detection method, which was calibrated with a series of polystyrene narrow standards (Polymer Laboratories). Elemental analyses were carried out by the Perkin Elmer 2400 CHN Elemental Analyzer for CHN analysis and by the Schöniger oxygen flask combustion method for anion analysis. UV–visible absorption spectra were measured by Hitachi U-2010 Double Beam UV/Visible Spectrophotometer. The absorbance of polymers was measured in solution in dichloromethane (spectrophotometric grade) at ambient temperature using rectangular quartz cuvettes (light path length = 10 mm) purchased from Sigma–Aldrich. Samples of pristine polymer thin films for UV–visible absorption spectra measurements were prepared by dip coating quartz plates into 1 mg cm^{-3} polymer solutions in dichloromethane (HPLC grade); and the measurements were carried out at ambient temperature. Photoluminescence spectra were obtained using Hitachi F-4500 Fluorescence Spectrophotometer equipped with Hamamatsu Photonics R928F Photomultiplier Tube (PMT). PL solution measurements were carried out using a Quartz Fluorescence Cuvette (light path length = 10 mm) purchased from Sigma–Aldrich.

Photoluminescence spectra measurements of the polymer solutions were carried out in dichloromethane (spectrophotometric grade) at 25 °C. Samples of pristine polymer thin films for PL spectra measurements were prepared by dip coating quartz plates into 0.1 mg cm^{-3} polymer solutions in dichloromethane (spectrophotometric grade), and the measurements were carried out at ambient temperature in air.

Cyclic voltammograms were recorded using a Princeton Applied Research Model 263A Potentiostat/Galvanostat. Measurements were carried out under argon at 25 ± 2 °C. A 10 cm^3 of tetrabutylammonium perchlorate ($TBAClO_4$) solution in acetonitrile (0.1 mol dm^{-3}) was used as the electrolyte solution. A three electrode system was used consisting of an Ag/Ag^+ reference electrode (silver wire in 0.01 mol dm^{-3} silver nitrate solution in the electrolyte solution), a platinum working electrode (2 mm-diameter smooth platinum disk, area = 3.14×10^{-2} cm^2), and a platinum counter electrode (platinum wire). Polymer thin films were formed by drop casting 1.0 mm^3 of polymer solutions in dichloromethane (HPLC grade) (1 mg cm^{-3}) onto the working electrode, then dried in air. Ferrocene was employed as a reference redox system according to IUPAC's recommendation [21].

All reactions were carried out under inert nitrogen atmosphere.

*1,4-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-benzene **1***

To a solution of 1,4-phenylenebisboronic acid (4.00 g, 24.13 mmol) in toluene (125 cm^3) pinacol was added (7.13 g, 60.33 mmol) and the mixture was heated at reflux for 3 h in the presence of molecular sieves 3 Å. The reaction mixture was allowed to cool to room temperature and then the toluene was removed in vacuo. The residue was purified by flash vacuum chromatography on silica gel 60—hexane/ethyl acetate (90/10). The residue was concentrated in vacuo to yield 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-benzene **1** as a white powder (7.20 g, 15.76 mmol, 65.3% yield). The product gave a single spot on TLC ($R_f = 0.55$) (petroleum ether/ethyl acetate (4/1)) and a single peak on GC (RT = 6.09 min). IR (solid state): 3091, 3000, 2983, 2932, 2368, 1520, 1462, 1435, 1392, 1380, 1370, 1342, 1324, 1269, 1250, 1210, 1166, 1140, 1098, 1020, 961, 942, 854, 822, 802, 680, 666, 622, 604, 596, 577, 569, 540, 536, 523, 512, 508, 495 cm^{-1}. Mass (EI); (*m*/*z*): 329, 330, 331 ($M^{\bullet +}$). ^{1}H-NMR ($CDCl_3$); δ_H/ppm: 1.27 (24H, s); 7.73 (4H, s). ^{13}C-NMR ($CDCl_3$), δ_C/ppm: 24.87 (8C); 83.84 (2C); 133.88 (4C). Anal. Calcd. for $C_{18}H_{28}B_2O_4$: C, 65.51; H, 8.55. Found: C, 65.23; H, 8.65.

Poly(2,7-(3,6-dimethyl-9-(2-hexyldecyl)-9H-carbazole-alt-p-phenylene) ***P1***

A solution of palladium (II) acetate (2.0 mg, 8.9 μmol) and tri-*p*-tolylphosphine (8.2 mg, 0.027 mmol) in toluene (3 cm^3) was stirred at 50 °C for 15 min in a sealed tube. After cooling to ambient temperature a solution of 2,7-dibromo-3,6-dimethyl-9-(2-hexyldecyl)-*9H*-carbazole (0.5278 g, 0.914 mmol) and 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaboralan-2-yl)-benzene (0.3092 g, 0.937 mmol) in toluene (7 cm^3) was added to the sealed tube and stirred at ambient temperature for 10 min. Then tetraethyl ammonium hydroxide (4 cm^3, 20% w/w in water, 5.43 mmol) was added and the mixture was heated at 120 °C with stirring for 72 h. The mixture was allowed to cool to ambient temperature and then bromobenzene (0.1 cm^3, 0.950 mmol) was added and the mixture stirred for a further 1 h at 120 °C. The mixture was again allowed to cool to ambient temperature and then phenylboronic acid (0.12 g, 0.984 mmol) was added and the mixture stirred for a further 1 h at 120 °C. After cooling to ambient temperature the mixture was worked up as in protocol 1 to give poly(2,7-(3,6-dimethyl-9-(2-hexyldecyl)-*9H*-carbazole-alt-*p*-phenylene) **P1** as a white powder (0.37 g, 83.3% yield). GPC: Mw = 25,000; Mn = 12,200; Mw/Mn = 2.0. ^{1}H-NMR ($CDCl_3$); δ_H/ppm: 0.66–.87 (6H, m); 0.99–1.43 (16H, m); 2.03–2.24 (1H, m); 2.48 (6H, s); 3.97–4.21 (2H, m); 7.23 (2H, s); 7.43 (4H, s); 7.91 (2H, s). Anal. Calcd. for $(C_{36}H_{47}N)_n$: C, 87.57; H, 9.59; N, 2.84. Found: C, 86.73; H, 9.19; N, 2.63; Br, 0.00.

Poly(2,7-(3,6-dimethyl-9-(2-hexyldecyl)-9H-carbazole-alt-2,5-difluoro-p-phenylene) ***P2***

A solution of palladium (II) acetate (2.0 mg, 8.9 μmol) tri-*p*-tolylphosphine (8.2 mg, 0.027 mmol) in toluene (3 cm^3) was stirred at 50 °C for 15 min in a sealed tube. After cooling to ambient temperature a solution of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,6-dimethyl-9-(2-hexyldecyl)-*9H*-carbazole (0.5216 g, 0.777 mmol) **1** and 1,4-dibromo-2,5-difluorobenzene (0.2062 g, 0.758 mmol) in toluene (7 cm^3) was added to the sealed tube and stirred at ambient temperature for 10 min. Then tetraethyl ammonium hydroxide (4 cm^3, 20% w/w in water, 5.43 mmol) was added and the mixture was heated at 120 °C with stirring for 72 h. The mixture was allowed to cool to ambient temperature and then bromobenzene (0.1 cm^3, 0.950 mmol) was added and the mixture stirred for a further 1 h at 120 °C. The mixture was again allowed to cool to ambient temperature and then phenylboronic acid (0.12 g, 0.984 mmol) was added and the mixture was stirred for further 1 h at 120 °C. After cooling to ambient temperature the mixture was poured onto methanol (500 cm^3). The precipitates were filtered off and dissolved in chloroform (200 cm^3). The insoluble materials in the chloroform solution were filtered off, and then the filtrate was concentrated in vacuo. The concentrated chloroform solution ($\sim$20 cm^3) was poured onto methanol (500 cm^3) and the precipitates filtered off and dried in vacuo to give poly(2,7-(3,6-dimethyl-9-(2-hexyldecyl)-*9H*-carbazole-alt-2,5-difluoro-*p*-phenylene) **P2** as a white powder (0.36 g, 91% yield). GPC: Mw = 11,200; Mn = 5,400; Mw/Mn = 2.1. 0.30 g of polymer **P2** was then fractionated by Soxhlet extraction with acetone for 24 h under an inert argon atmosphere. After 24 h, the Soxhlet extraction system was allowed to cool to ambient temperature. The insoluble fraction in hot acetone was dissolved in a small amount of chloroform ($\sim$20 cm^3), which was then poured onto methanol (500 cm^3) and stirred for 24 h. The precipitate was filtered off and dried in vacuo to afford polymer **P2** as a white powder (0.13 g, 43% of initial weight). GPC: Mw = 13,000; Mn = 7,000; Mw/Mn = 1.9. IR (solid state): 2929, 2923, 2853, 2358, 1612, 1509, 1471, 1460, 1403, 1378, 1354, 1291, 1271, 1243, 1166, 1105, 1032, 999, 887, 870, 854, 790, 764, 721, 698, 620, 583, 575, 540, 524, 508, 497 cm^{-1}. ^{1}H-NMR ($CDCl_3$); δ_H/ppm: 0.74–0.92 (6H, m); 1.08–1.50 (16H, m); 2.13–2.30 (1H, m); 2.50 (6H, s); 4.17 (2H, m); 7.15 (2H, m); 7.30 (2H, s); 8.01 (2H, s). ^{13}C-NMR ($CDCl_3$), δ_C/ppm: 14.09 (2C); 20.16 (1C); 22.60 (1C); 22.63 (2C); 26.31 (1C); 26.39 (1C); 29.25 (1C); 29.48 (1C); 29.62 (2C); 29.96 (1C); 31.68 (1C); 31.77 (1C); 31.83 (1C); 37.69 (1C); 48.03 (1C); 110.39 (2C); 117.51 (2C); 121.39 (2C); 122.61 (2C); 126.84 (2C); 130.06 (2C); 132.55 (2C); 139.93 (2C); 155.45 (d, $^1J_{C–F}$ = 242 Hz, 2C). Anal. Calcd. for $(C_{36}H_{45}NF_2)_n$: C, 81.62; H, 8.56; N, 2.64. Found: C, 81.00; H, 8.37; N, 2.55; Br, 0.00.

Poly(2,7-(3,6-dimethyl-9-(2-hexyldecyl)-9H-carbazole-alt-tetrafluoro-p-phenylene) ***P3***

Poly(2,7-(3,6-dimethyl-9-(2-hexyldecyl)-*9H*-carbazole-alt-tetrafluoro-*p*-phenylene) **P3** was prepared according to the preparation of **P2** except that 0.5105 g (0.760 mmol) of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3,6-dimethyl-9-(2-hexyldecyl)-*9H*-carbazole **1** and 0.2285 g (0.742 mmol) of 1,4-dibromo-tetrafluorobenzene were used. Poly(2,7-(3,6-dimethyl-9-(2-hexyldecyl)-*9H*-carbazole-alt-tetra-*p*-phenylene) **P3** was obtained as a white powder (0.38 g, 91.7% yield).

GPC: Mw = 13,300; Mn = 6,600; Mw/Mn = 2.5. 0.35 g of polymer **P3** was then fractionated by Soxhlet extraction with acetone for 24 h under an inert argon atmosphere. After 24 h, the Soxhlet extraction system was allowed to cool to ambient temperature. The insoluble fraction in hot acetone was dissolved in a small amount of chloroform ($\sim$20 cm^3), which was then poured onto methanol (500 cm^3) and stirred for 24 h. The precipitate was filtered off and dried in vacuo to afford polymer **P3** as a white powder (0.07 g, 20% of initial weight). GPC: Mw = 24,100; Mn = 15,100; Mw/Mn = 1.6. IR (solid state): 2929, 2924, 2853, 1613, 1457, 1379, 1354, 1307, 1289, 1244, 1213, 1171, 1102, 1036, 999, 975, 938, 870, 851, 784, 722, 691, 662, 620, 596, 582, 571, 553, 532, 514, 504, 486 cm^{-1}. ^{1}H-NMR ($CDCl_3$); δ_H/ppm: 0.63–0.86 (6H, m); 0.97–1.42 (16H, m); 2.00–2.22 (1H, m); 2.41 (6H, s); 4.11 (2H, m); 7.29 (2H, s); 8.05 (2H, s). ^{13}C-NMR ($CDCl_3$), δ_C/ppm: 14.05 (1C); 14.08 (1C); 19.89 (1C); 19.98 (1C); 22.59 (1C); 22.63 (2C); 26.41 (1C); 29.23 (2C); 29.46 (1C); 29.87 (1C); 31.75 (2C); 31.83 (2C); 37.71 (1C); 48.05 (1C); 111.20 (2C); 120.11 (2C); 121.84 (2C); 123.36 (2C); 124.91 (2C); 127.43 (2C); 139.87 (2C); 144.01 (m, 4C). Anal. Calcd. for $(C_{36}H_{43}NF_4)_n$: C, 76.43; H, 7.66; N, 2.48. Found: C, 76.08; H, 7.70; N, 2.32; Br, 0.00.

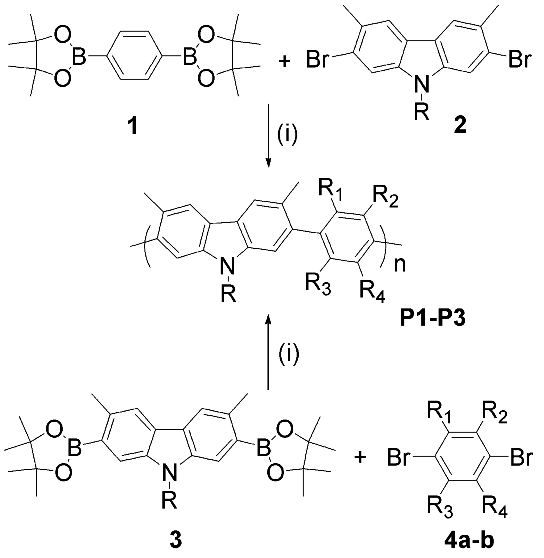
Results and discussion

Synthesis and characterization

The preparation of polymers **P1**–**P3** is outlined in Scheme 1. Polymer **P1** was obtained in good yields upon reaction of 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-benzene **1** with the carbazole dibromide **2** via a Suzuki type cross coupling condensation polymerization reaction in toluene, using tetraethyl ammonium hydroxide in water as a base and a mixture of palladium(II) acetate together with tri-*p*-tolylphosphine as catalyst. Polymers **P2** and **P3** were also obtained in good yields using similar reaction conditions starting from the carbazole bis boronate ester **3** and dibromides **4a** and **4b**, respectively. The average molecular weights as measured by gel permeation chromatography using polystyrene standards of the three polymers are shown in Table 1.

The proposed structure of the polymers is confirmed by NMR spectroscopy. The aromatic region of the ^{1}H-NMR spectra of polymer **P1** showed three broad signals at 7.91, 7.43, and 7.23 ppm corresponding, respectively, to hydrogens at the 1,8-positions of carbazole repeat units, hydrogens on the phenylene repeat units, and hydrogens on the 4,5-positions of carbazole repeat units. The aliphatic region of the ^{1}H-NMR spectra show features of the branched alkyl chains including a broad doublet at ca. δ 4.10 due to the methylene group attached directly to the nitrogen of the carbazole ring, as well as a signal at ca. δ 2.48 due to the 3,6-methyl groups on the carbazole ring. The aromatic region of the ^{13}C-NMR spectra of polymer **P1** showed eight main peaks, six of which were assigned to the carbons of the carbazole ring and the other two to the carbons of the phenylene ring.

Polymer **P2** displayed three main signals in the aromatic region of its ^{1}H-NMR spectrum with the first two signals at 8.01 and 7.30 ppm as broad singlets corresponding, respectively, to hydrogens at 1,8-positions and 4,5-positions of carbazole repeat units. The hydrogens of the bis-fluorophenylene repeat units give a multiplet at 7.15 ppm as a result of coupling with adjacent fluorine substituents. The aliphatic region of the ^{1}H-NMR spectra show features of the branched alkyl chains including a broad doublet at 4.17 due to the methylene group attached directly to the nitrogen of the carbazole ring, as well as a signal at 2.50 due to the 3,6-methyl groups on the carbazole ring. The aromatic region of the ^{13}C-NMR spectra of **P2** showed nine main signals. Six of the main signals were assigned to the carbons of the carbazole ring as singlets. The other three aromatic signals were a doublet and two multiplets and were assigned to the carbons of the phenylene repeat units. Polymer **P3** displayed two broad singlets at 8.05 and 7.29 ppm in the aromatic region of its ^{1}H-NMR spectrum corresponding, respectively, to hydrogens at 1,8-positions and 4,5-positions of carbazole repeat units. The aliphatic region of the ^{1}H-NMR spectra show features of the branched alkyl chains including a broad doublet at 4.11 due to the methylene group attached directly to the nitrogen of the carbazole ring, as well as a signal at 2.41 due to the 3,6-methyl groups on the carbazole ring. The aromatic region of the ^{13}C-NMR spectra of **P3** showed eight main signals, six of which were assigned to the carbons of the carbazole ring as singlets and the other two aromatic signals were assigned to the carbons of the phenylene repeat units.



P1, $R_1 = R_2 = R_3 = R_4 = H$
P2, $R_1 = R_4 = H$, $R_2 = R_3 = F$
P3, $R_1 = R_2 = R_3 = R_4 = F$
R = 2-hexyldecyl.

Scheme 1 (i) **a** $Pd((OAc)_2/P(p\text{-tolyl})_3$, NEt_4OH, toluene/H_2O; **b** $PhB(OH)_2$; and **c** PhBr

The thermal stability of the polymers was investigated in this study. Thermal gravimetric analysis (TGA)

Table 1 Molecular weight distributions, UV–visible, and PL data of **P1**, **P2**, and **P3**

Polymer	Mn	Mw	Absorption		PL emission		Stokes shift (nm)
			λ_{max} (nm) (CH_2Cl_2)	λ_{max} (nm) (film)	λ_{max} (nm) (CH_2Cl_2)	λ_{max} (nm) (film)	
P1	12200	25000	329 (358)	328 (363)	407	407	79
P2	7000	12900	321 (359)	323 (365)	404	411	88
P3	15100	24100	317 (354)	319 (368)	399	402	83

Numbers in brackets correspond to shoulder absorption peaks

measurements revealed the remarkable stability of the polymers up to 420 °C. The subsequent degradation and weight loss of the polymers beyond 420 °C was proportional to the mass of the alkyl-group substituents for polymer **P1** up to a temperature of 800 °C; and, however, it was more pronounced for polymers **P2** and **P3** which indicates degradation pathways involving the loss of both fluorine as well as alkyl substituents above 420 °C for the latter two polymers.

Solution and solid-state electronic spectra

Figure 1a shows the absorption spectra of polymers **P1**–**P3** in dichloromethane solutions. Polymer **P1** displays an absorption band at 329 nm with a shoulder absorption band at 358 nm. These absorption values are higher than those of 3,6-linked carbazole main chain polymers [22, 23] (~308 nm) indicating a greater electronic conjugation in polymer **P1**, as a result of its linkage through the 2,7-positions of the carbazole repeat units. Polymers **P2** and **P3** display blue shifted emission bands with respect to polymer **P1**, respectively, at 321 and 317 nm, together with shoulder absorption bands at 359 and 354 nm (Table 1). This trend clearly indicates the effect of steric hindrance exerted by the fluorine substituents on polymers **P2** and **P3** which causes the gradual twisting of the polymer chains out of conjugation. The shoulder absorption bands in all three polymers could be explained by the existence of segments of more extended electronic conjugation along the polymer chains. Figure 1b shows the absorption spectra of polymers **P1**–**P3**. There is little difference in the values of the absorption maxima of the three polymers between solution and solid state, however, the intensity of the shoulder peaks is clearly more prominent in films than it is in solution indicating that the polymer chains adopt more planar conformations in the solid state. Out of the three polymers the shoulder absorption band on polymer **P2** is the most intense. We believe that this is due to a donor acceptor effect between the 3,6-dimethyl-carbazole repeat units and the difluoro-phenylene repeat units in **P2**. The shoulder absorption band is also prominent in polymer **P3** in the solid state; however, it is less intense than that observed for **P2**, indicating that there is a balance between the donor/acceptor effects on the one hand and the steric effects of the fluorine substituents on the phenylene repeat units on the other hand. The band gap of polymer **P1** as established from the onset of its absorption in the solid state was estimated at an E_g value of 3.2 eV (Table 2). A narrower band gap of 3.16 eV was observed for both polymers **P2** and **P3**.

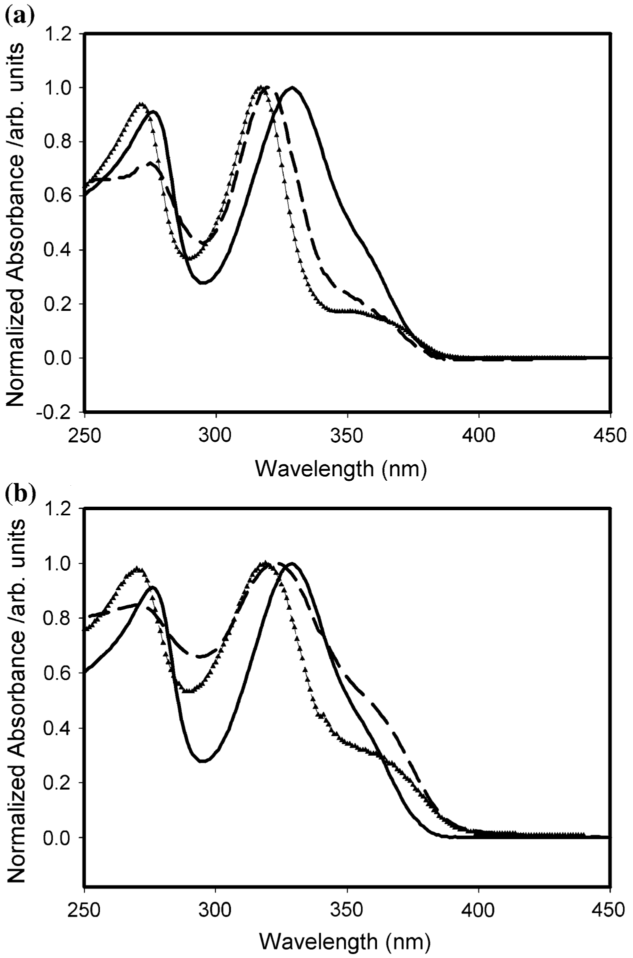


Fig. 1 **a** UV spectra of **P1** (*solid line*), **P2** (*dashed line*), and **P3** (*triangles*) in dichloromethane. **b** UV spectra of films of **P1** (*solid line*), **P2** (*dashed line*), and **P3** (*triangles*)

Solution and solid-state fluorescence spectra

Fluorescence studies on polymers **P1**–**P3** were performed both in solution in dichloromethane and in the solid state.

Table 2 Cyclic voltammetry results and band gaps of **P1**, **P2**, and **P3**

Polymer	E_{pa}^{a}/V	E_{pc}^{a}/V	I_{p}^{c}/eV	Band gap E_{g}^{d}/eV
P1	–[b]	0.81	5.52	3.20
P2	–[b]	0.90	5.63	3.16
P3	–[b]	0.89	5.62	3.16

[a] Versus (Ag/Ag$^+$)

[b] Ill defined oxidation wave

[c] Ionization potential (versus vacuum) determined from onset of oxidation

[d] Band gap estimated from the onset position of the absorption band

The results of these studies are summarized in Table 1. The polymers show emission bands between 399 and 407 nm in solution in dichloromethane and between 402 and 411 nm in films (Fig. 2). The emission spectra are blue shifted in comparison with those from poly(9-alkyl-*9H*-carbazole-3,6-diyl)s (~425 nm) [22, 23] and are similar to those of poly(3,6-dimethyl-9-alkyl-*9H*-carbazole-2,7-diyl)s (~397 nm) [16]. The Stokes shifts are between 79 and 88 nm which are of the same order as those of poly(3,6-dimethyl-9-alkyl-*9H*-carbazole-2,7-diyl)s [16] and point to large structural differences between the ground and excited states in these materials both in solution and in the solid state.

Electrochemical studies

Investigations of the electrochemical properties of polymers **P1**–**P3** were conducted, using cyclic voltammetry measurements on drop-cast polymer films in acetonitrile with tetrabutylammonium perchlorate as an electrolyte. The cyclic voltammogram of the polymers are shown in Fig. 3. Their redox potentials as well as their ionization potentials (versus vacuum) are shown in Table 2.

The redox behavior of all three polymers indicates quasi reversible redox waves with ill-defined oxidation waves and associated reduction waves at a potential E_{pc} at 0.81 V for polymer **P1** and at 0.90 and 0.89 V, respectively, for **P2** and **P3**. The ionization potential (versus vacuum) of polymer **P1** as estimated from the onset of its oxidation in cyclic voltammetry experiments is found at 5.52 eV (on the basis that ferrocene/ferrocenium is 4.8 eV below the vacuum level [24]). Higher ionization potentials were observed for polymers **P2** and **P3** (5.63 and 5.62 eV, respectively).The higher ionization potential values of **P2** and **P3** are a consequence of the presence of the electron withdrawing fluorine substituents on the alternate phenylene repeat units on their polymer chains. It must also be noted that the ionization potential values of all three polymers are still lower than that of poly(9,9-dioctyl-fluorene-2,7-diyl) (5.8 eV) [25], which could suggest an easier hole injection into films of these polymers from ITO electrodes and their potential use in electronic device applications.

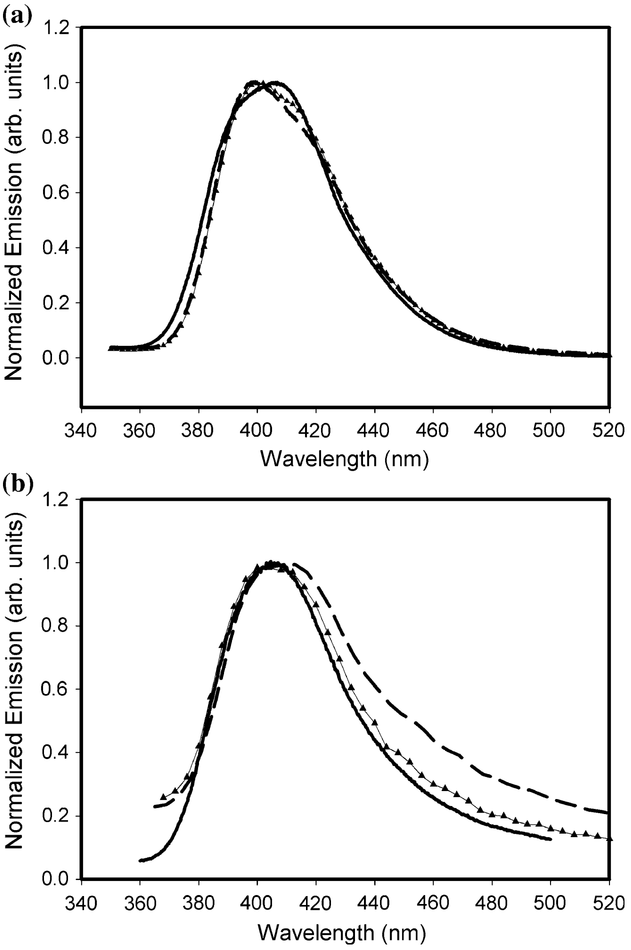


Fig. 2 **a** PL spectra of **P1** (*solid line*), **P2** (*dashed line*), and **P3** (*triangles*) in dichloromethane. **b** PL spectra of films of **P1** (*solid line*), **P2** (*dashed line*), and **P3** (*triangles*)

Conclusion

The preparation and characterization of new classes of blue emitting conjugated polymers comprising 2,7-linked 3,6-dimethyl-9-alkyl carbazole units and 1,4-phenylene units with varying number of fluorine substituents has been realized. The polymers were prepared through Suzuki coupling methodologies. All three polymers are thermally stable up to 420 °C. Copolymers **P2** and **P3** which have, respectively, two and four fluorine substituents on their alternate phenylene repeat units have lower band gaps (3.16 eV) than that of copolymer **P1** which has no fluorine substituent on its phenylene repeat units (3.2 eV) as a result of the donor/acceptor effect of the different alternating units in this series of copolymers. Polymers **P1–P3** emit in the blue part of the electromagnetic spectrum in solution in dichloromethane

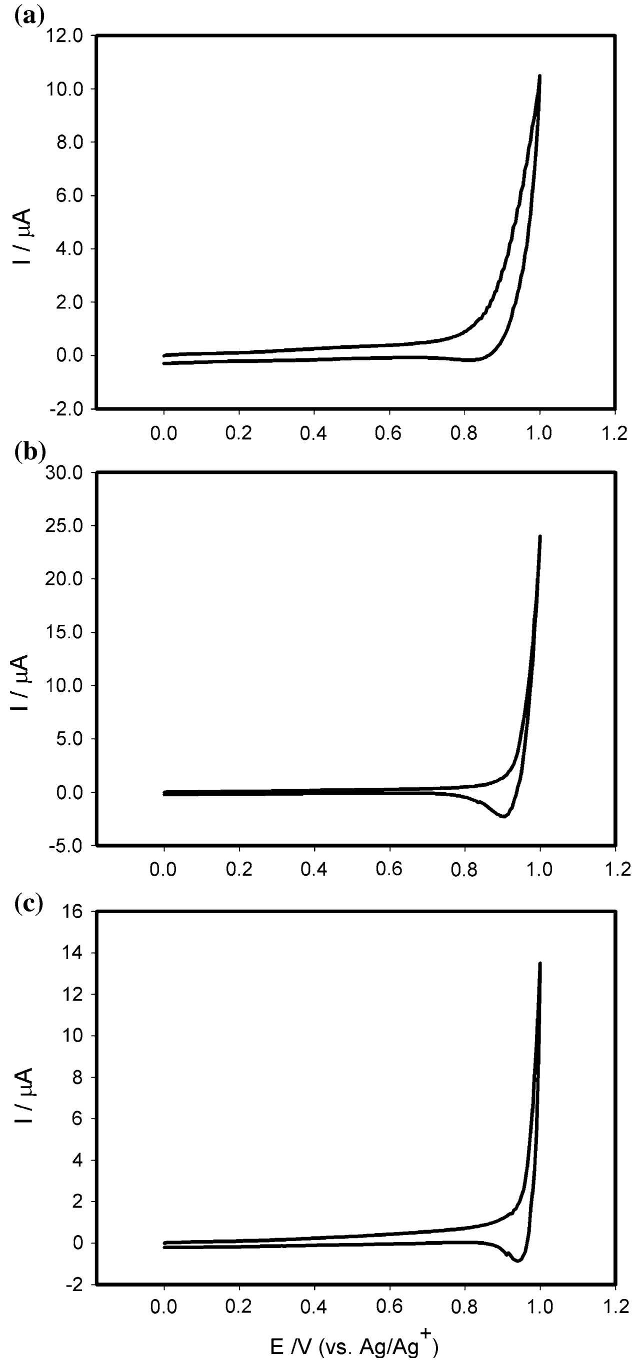


Fig. 3 Cyclic voltammetry curves of thin films of **a P1**, **b P2**, and **c P3** on platinum disk electrodes (area 0.031 cm^2) at a scan rate of 100 mV s^{-1} in acetonitrile/tetra butyl ammonium perchlorate (0.1 mol dm^{-3})

(between 399 and 407 nm) as well as in films (between 402 and 411 nm). The polymers were also shown to be electrolytically stable. The ionization potential of polymers **P2** and **P3** were found to be higher than that of **P1** as a result of their substitution with the electron withdrawing fluorine groups. Investigation of the electroluminescent properties of the new materials is currently underway.

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