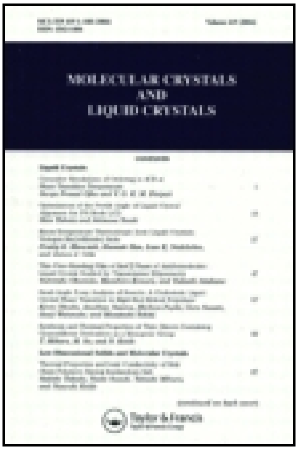

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N-Aryl 2,7-Linked Carbazole Polymers and Copolymers with Fluorine Protecting Groups: A New Class of Blue Emitting Polymers for LED Applications

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N-Aryl 2,7-Linked Carbazole Polymers and Copolymers with Fluorine Protecting Groups: A New Class of Blue Emitting Polymers for LED Applications

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N-functionalisation of 3,6-difluoro 2,7-linked carbazole polymers with aryl substituents affords blue emitting materials with good electrolytic stability and moderate quantum yields of fluorescence. Copolymers comprising N-aryl 2,7-linked carbazole repeat units with 3,6-fluoro protecting groups and triaryl amine repeat units afford blue emitting materials with enhanced electrolytic stability and high quantum yields of fluorescence. Both classes of materials were prepared using Suzuki cross-coupling polymerisation methods. The synthesis and characterisation of this new class of materials together with a study of their electrochemical and photophysical properties is presented.

Keywords: charge transport; conjugated polymers; light emitting diodes

INTRODUCTION

Development of new highly fluorescent blue light emitting polymers is attracting much research interest since such materials could be used as active layers in light emitting diodes either as blue emitters or as energy-transfer donors and hosts for 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]. Carbazole materials are used extensively in this research area either as hole-transporting materials [3], or as wide band gap hosts to various fluorophores [4]. Poly(9-alkyl-9*H*-carbazole-3,6-diyl)s constitute another class of carbazole-based materials that has also been targeted in the literature [5]. This class of carbazole polymers differs from polymers such as poly(vinylcarbazole), since these are main-chain carbazole polymers rather than linear polymers with pendent carbazole units.

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However, in view of their structural make-up and 3,6-linkage between consecutive carbazole repeat units, electronic conjugation in poly(9-alkyl-9*H*-carbazole-3,6-diyl)s is limited to about two carbazole units, in addition, their quantum yields of fluorescence are fairly low.

Recently, there has been much effort in developing alternative polymers to polyfluorene derivatives for application in light emitting diodes. A special interest has focused on 2,7–linked carbazole polymers[6]. We have shown that poly(9-alkyl-*9H*-carbazole-2,7-diyl)s [7] offer many attractive properties such as high quantum yields of fluorescence and lower oxidation potentials than their polyfluorene analogues. These polymers also emit in the blue part of the electromagnetic spectrum, however, cyclic voltammetry studies on this class of polymers have revealed that they do oxidize irreversibly under electrolytic conditions. This instability arises as the result of the high reactivity of their unprotected 3,6-positions [8]. We have demonstrated in earlier works that the protection of these positions in 2,7-linked 9-alkyl carbazole polymers with methyl [9] or fluoro [10] substituents allowed the preparation of materials of much higher electrolytic stability. We have also shown [11] how the functionalisation of 2,7-linked carbazole polymers with arylamine substituents imparts different electronic properties to the resulting materials. In this contribution, we present our results on the preparation of 2,7-linked-9-aryl-*9H*-carbazole polymers and alternating copolymers where the 3,6-positions of the carbazole repeat units are functionalized with fluorine substituents and present a study of their electrical and photophysical properties.

EXPERIMENTAL SECTION

Materials: (4-Butyl-phenyl)-bis-[4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenyl]-amine was prepared according to literature procedures [10]. All other reagents were obtained from commercial sources and used as received. Tetrahydrofuran (THF) was distilled over sodium-benzophenone under inert nitrogen atmosphere. DMF was distilled over calcium hydride 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 3A.

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 or acetone-d_6 solutions with TMS as the internal standard. IR absorption spectra were recorded on the Nicolet Model 205 FT-IR Spectrometer. Liquid samples were analysed neat, using NaCl–plate method and solid samples were analysed using the

Diamond ATR attachment for solid samples. Melting points were obtained using Gallenkamp Melting Point Apparatus. GC-MS spectra were recorded on Perkin Elmer Turbomass Mass Spectrometer equipped with Perkin Elmer PE-5MS Capillary Column. Mass spectra were obtained by the electron impact method (EI) or the chemical ionization method (CI). 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 $minute^{-1}$. 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 spectrophotometric grade solvents (toluene) 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 harmine, and quinine sulfate dihydrate solutions were carried out in respectively 0.05 mol m^{-3} and 0.5 mol dm^{-3} sulfuric acid at 25°C in the air since both harmine and quinine sulfate dihydrate exhibit no oxygen quenching effect.

Photoluminescence spectra measurements of the polymer solutions were carried out in spectrophotometric grade toluene 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 (HPLC grade), and the measurements were carried out at ambient temperature in air.

Absorbances at employed excitation wavelengths of the sample solutions were kept below 0.05 to obtain inner-filter-effect-free photoluminescence spectra. All photoluminescence spectra were corrected.

Cyclic voltammograms were recorded using a Princeton Applied Research Model 263A Potentiostat/Galvanostat. Measurements were carried out under argon at 25 ± 2°C. 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 disc, area $= 3.14 \times 10^{-2}$ 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 [12].

Synthesis: All reactions were carried out under inert nitrogen atmosphere.

2,7-Dibromo-9-(4-(2-butyloctyloxy)phenyl)-3,6-difluoro-9H-carbazole 2

2,7-Dibromo-3,6-difluoro-*9H*-carbazole (1.5 g, 4.12 mmol) was dissolved in dry toluene (50 cm^3), to which 1-(2-butyl-octyloxy)-4-iodo-benzene (2.1 g 5.40 mmol), 1,2-diaminocyclohexane (0.095 g, 0.83 mmol), K_3PO_4 (1.85 g, 8.73 mmol) and CuI (0.04 g, 0.21 mmol) was added. The reaction was kept at reflux for 3 days whilst monitored *via* TLC analysis. The reaction was cooled to room temperature and H_2O (150 cm^3) was added. The product was extracted with dichloromethane (2×100 cm^3), dried over $MgSO_4$ and the solvent removed *in vacuo*. The product was then purified by silica gel column chromatography, eluted with 20:1 40–60 petroleum ether: dichloromethane to give white crystals (0.97 g, 46.47% yield). The product gave a single spot on TLC ($R_f = 0.36$) 20:1 40–60 petroleum ether: dichloromethane, m.p. 146.2–148°C. Mass (EI); (m/z): 619, 621, 623 ($M^{\bullet+}$). ^1H NMR ($CDCl_3$) δ_H/ppm: 0.94 (t, 6H, $J = 8.79$ Hz); 1.35 (m, 16H); 1.88 (m, 1H); 3.96 (d, 2H, $J = 5.96$ Hz); 7.13 (d, 2H, $J = 8.79$ Hz); 7.36 (d, 2H, $J = 8.48$ Hz); 7.45 (d, 2H, $J = 5.34$ Hz), 7.76 (d, 2H, $J = 8.16$ Hz). ^{13}C NMR ($CDCl_3$) δ_C/ppm: 14.09; 22.69; 23.07; 26.88; 29.13; 29.70; 31.13; 31.45; 31.87; 38.02; 71.41; 107.08 (d, $J = 25$ Hz); 108.37 (d, $J = 24$ Hz); 114.34; 116.07, 121.74; 121.81, 155.65 (d, $J = 247$ Hz); 159.53.IR (cm^{-1}): 2956, 2923, 2852, 1570, 1514, 1460, 1445, 1379, 1333, 1296, 1251, 1187, 1146, 1164, 1146, 1112, 1039, 1014, 994, 978, 956, 917, 869, 858, 833, 811, 747, 718, 693, 672, 643, 626, 611, 582. Elemental analysis calculated for $C_{30}H_{33}NOBr_2F_2$: C, 57.99; H, 5.35; N, 2.25; Br, 25.72. Found: C, 58.18; H, 5.36; N, 2.19; Br, 25.44.

Poly(3,6-difluoro-9-(4-(2-butyloctyloxy)phenyl)-9H-carbazole-2,7-diyl) P1

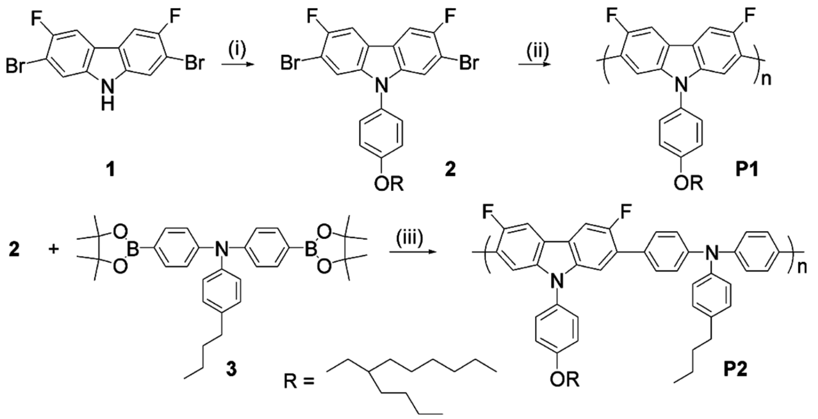
2,7-Dibromo-9-(4-(2-butyloctyloxy)phenyl)-3,6-difluoro-9H-carbazole (0.30 g, 0.483 mmol), bis(pinacolato)diboron (0.123 g, 0.483 mmol), potassium acetate (0.081 g, 0.821 mmol), Pd(dppf)Cl_2(7.8 mg, 0.009 mmol) were degassed under argon and DMF (4 cm^3) was added and the mixture was heated at 100°C overnight. The mixture was then cooled to room temperature and THF (10 cm^3), deoxygenated water (4 cm^3) and $NaHCO_3$ (0.284 g, 3.38 mmol) were added, and the mixture refluxed for 48 hrs. The reaction was cooled to room temperature and 5-bromo-m-xylene (0.089 g, 0.483 mmol) was added and heated to reflux for 2 hrs. Again the reaction was cooled to room temperature and 3,5-dimethylphenylboronic acid (0.145 g, 0.966 mmol) was added and heated to reflux for another 2 hrs. The reaction mixture was cooled to room temperature, and poured onto chloroform (300 cm^3) which was washed with water (200 cm^3) and dried over $MgSO_4$. The solvent was concentrated *in vacuo* to a volume of $\sim$5 cm^3 and precipitated in methanol (500 cm^3). The polymer was collected *via* filtration under an argon atmosphere, then dissolved in toluene and filtered through a short silica plug. The solvent was concentrated *in vacuo* to $\sim$5 cm^3 and precipitated in methanol (500 cm^3), filtered under and argon atmosphere and dried under vacuum to afford polymer **P1** as an ivory powder (79 mg, 35.50% yield). Mn = 4,400, Mw = 6,400, PD = 1.45. ^{1}H NMR ($CDCl_3$); δ_H/ppm: 0.80–0.94 (m, 6H); 1.22–1.53 (m, 16H); 1.74 (m, H); 3.82–3.92 (m, 2H); 7.048 (m, 2H); 7.310 (m, 2H); 7.410 (m, 2H); 7.831 (m, 2H). ^{13}C NMR ($CDCl_3$), δ_C/ppm: 14.08; 22.65; 23.019; 26.81; 29.04; 30.89; 31.03; 31.39; 31.81; 37.96; 71.19; 106.301 (m); 115.73; 122.62; 123.32; 128.41; 129.39; 129.41; 138.54; 154.85 (d, $J = 241$ Hz); 158.86. Elemental Analysis calculated for $C_{30}H_{33}NOF_2$: C, 78.06; H, 7.21; N, 3.03; Br, 0. Found: C, 76.69; H, 7.32; N, 2.74; Br, 0.

Poly(3,6-difluoro-9-(4-(2-butyloctyloxy)phenyl)-9H-carbazole-2,7-diyl-alt-N-(4″-butylphenyl)imino (1,1′-diphenyl-4,4′-diyl) P2

To a solution of 2,7-dibromo-9-(4-(2-butyloctyloxy)phenyl)-3,6-difluoro-*9H*-carbazole (0.30 g, 0.483 mmol), (4-butyl-phenyl)-bis-[4-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-phenyl]-amine (0.233 g, 0.483 mmol) in dry toluene (10 cm^3) was added $Pd(OAc)_2$ (7 mg, 0.031 mmol), mmol), tri-*p*-tolylphosphine (19 mg, 0.062 mmol) and stirred for 10 mins. To this was added deoxygenated tetraethylammonium hydroxide (3.2 cm^3 of 20% aq. solution), the mixture was then refluxed for 24 hours. After cooling the polymer was end-capped with the addition of 5-bromo-m-xylene (0.1 cm^3) and refluxed for 3 hrs at 120°C. After cooling 3,5-dimethyl phenyl boronic acid (0.15 g) was added and again the reaction was heated to 120°C for 3 hours. The reaction mixture was cooled to room temperature, and then poured into methanol (500 cm^3). The methanol solution was stirred overnight and then filtered through a membrane filter. The collected solid was dissolved in $CHCl_3$(500 cm^3) then filtered and the filtrate was concentrated to about ~5 cm^3 and then precipitated in methanol (500 cm^3) overnight and then collected by filtration. The polymer was then clean using a Soxhlet extraction with methanol (18 hrs) then acetone (18 hrs) and then solubilised in chloroform. This was then concentrated to about ~5 cm^3 and then precipitated in methanol (500 cm^3) and collected by filtration to afford the polymer as a yellow powder (237 mg, 81% yield). Mn = 11400, Mw = 20200, PD = 1.77. ^{1}H NMR ($CDCl_3$); δ_H/ppm: 0.89–1.02 (m, 9H); 1.33–1.68 (m, 20H); 1.86 (m, H); 2.62 (m, 2H); 3.94 (d, 2H, $J = 6.11$ Hz); 7.13 (d, 6H, $J = 9.3$ Hz); 7.20 (d, 6H, $J = 8.55$); 7.32 (d, 2H, $J = 5.38$), 7.48 (m, 4H), 7.82 (d, 2H, $J = 11.74$). ^{13}C NMR ($CDCl_3$), δ_C/ppm: 13.978 (C); 14.11 (2C); 22.41 (C); 22.68 (C); 23.07 (C); 26.87 (C); 29.11 (C); 29.69 (C); 31.41 (C); 31.86 (C); 33.66 (2C); 35.11 (m, 2C); 38.01 (2C); 71.23 (C); 106.61 (d, 2C, $J = 27.83$ Hz); 110.589 (2C); 115.79 (2C); 121.65 (m, 2C); 122.65 (2C), 122.86 (4C), 123.13 (2C), 125.08 (2C), 125.47 (2C), 127.78 (2C), 128.53 (2C), 129.18 (2C), 129.27 (C), 129.93 (2C), 130 (2C), 130.45 (2C), 138.59 (C), 139.13 (2C), 144.79 (C), 147.16 (2C), 154.85 (d, 2C, $J = 238.96$ Hz); 158.95 (2C). ^{19}F NMR ($CDCl_3$) δ_F/ppm: − 127.52 (m, 2F). Elemental Analysis calculated for $C_{52}H_{54}N_2OF_2$: C, 82.07; H, 7.15; N, 3.68; Br, 0. Found: C, 82.00; H, 7.09; N, 3.29, Br, 0.

RESULTS AND DISCUSSIONS

The preparation of poly(3,6-difluoro-9-(4-(2-butyloctyloxy)phenyl)-*9H*-carbazole-2,7-diyl) **P1** is depicted in Scheme 1. 2,7-Dibromo-9-(4-(2-butyloctyloxy)phenyl)-3,6-difluoro-*9H*-carbazole **2** was prepared through a copper catalysed arylation reaction of carbazole **1** using Cu(I) iodide and 1,2-diaminocyclohexane and was obtained in 47% yield. Attempts to prepare the bis boronic ester derivative from **2** proved problematic since even though borylation of **2** using a palladium catalysed reaction associating **2** and bis(pinacolato)diboron according to established literature methods [13] did afford the desired product, its purification from excess bis(pinacolato) diboron and other contaminants proved extremely difficult upon using various chromatographic



SCHEME 1 (i) Toluene, 1-(2-butyl-octyloxy)-4-iodo-benzene, 1,2-diaminocyclohexane, K_3PO_4, CuI; (ii) (a) Bis(pinacolato)diboron, KOAc, $Pd(dppf)Cl_2$, DMF, (b) $NaHCO_3$, THF/H_2O, (c) 5-bromo-*m*-xylene, d) 3,5-dimethylphenylboronic acid; (iii) (a) Toluene , $Pd(OAc)_2$, tri-*p*-tolylphosphine, Tetraethylammonium hydroxide, (b) 3,5-Dimethylphenylboronic acid, (c) 5-bromo-*m*-xylene.

conditions (including the use of various solvents and organic bases as co-eluents), as a result of its decomposition on chromatographic supports. Similar difficulties were observed in previous work in the purification of bis-boronic ester derivatives of 9-alkyl-3,6-difluoro-*9H*-carbazole [10]. In light of the problems for the separation of the bis boronic ester from monomer **2**, it was decided to prepare polymer **P1** in a one-pot reaction using equimolar amounts of monomer **2** and bis(pinacolato)diboron and potassium acetate as a base in a first stage followed by addition of a stronger base in a second stage to undertake the polymerization reaction. Polymer **P1** was hence obtained in 36% yield. Preparation of alternating copolymer **P2** (Scheme 1) was undertaken through a Suzuki cross-coupling polymerisation reaction using monomer **2** and triaryl amine bis boronate ester derivative **3**. Polymer **P2** was obtained in 81% yield. Gel permeation chromatography results from these polymerization reactions (using polystyrene standards) have shown weight average molecular weight values of 6,400 Da for polymer **P1** and 20,200 Da for copolymer **P2**.

NMR studies conducted in chloroform, on polymer **P1** confirmed its assigned structure and linkage of the carbazole repeat units at the 2,7-positions. ^1H NMR studies, reveal in the aromatic region, four broad multiplets with equal integral intensities, centred around 7.83, 7.41, 7.31, and 7.05 ppm, corresponding to the two chemical environments of hydrogens at the 1- and 8-positions and the 4- and 5-positions of carbazole rings and the two other hydrogen environments of the aryl substituents. In addition a broad peak centred around 3.85 ppm, corresponding to hydrogens of the methylene groups directly attached to the oxygen of the aryl ring, was observed together with other signals from the rest of alkyl chains. ^{13}C NMR studies on polymer **P1** reveal ten chemical environments in the aromatic region at around 106.3; 115.7; 122.6; 123.3; 128.4; 129.4; 129.4; 138.5; 154.8; 158.86. NMR studies on copolymer **P2** also confirm its assigned structure.

SOLUTION AND SOLID-STATE ELECTRONIC SPECTRA

Figure 1 shows the absorption spectra of polymer **P1** both in solution and in the solid-state (Film). The polymer displays a maximum absorption in solution (Toluene) at a $\lambda_{\max}$ value of 333 nm with a shoulder absorption band at 372 nm (Table 1). The shoulder absorption could be explained by the existence of segments of more extended electronic conjugation along the polymer chains. The absorption maxima values of polymer **P1** are blue shifted when compared with those of the equivalent 2,7-linked 9-aryl-carbazole polymers [14] with no protecting groups at the 3,6-position (333 and 372 nm for **P1** *vs.* 387 nm for the unprotected polymer). Its electronic delocalisation is however, similar to that of 2,7-linked 3,6-difluoro-9-alkyl carbazole polymers we reported in a previous study [10]. These results indicate that **P1** has a reasonable electronic conjugation when compared to

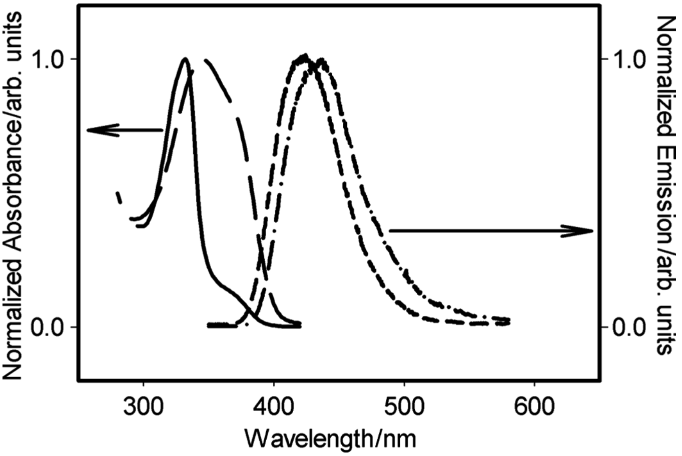


FIGURE 1 UV spectra of polymer **P1** in toluene (solid line), and as a film (long dashed line). PL spectra of **P1** in toluene (short dashed line) and as a film (dashed dot line).

TABLE 1 UV-Vis Data, Fluorescence Data, Redox Potentials (vs. Ag/Ag$^+$) and Quantum Yields of Fluorescence of Polymers **P1** and **P2**

	Absorption		Emission							
Polymer	λ_{max}/nm (Toluene)	λ_{max}/nm (Film)	λ_{max}/nm (Toluene)	λ_{max}/nm (Film)	Stokes shift/nm	Band Gap^a/eV	E_{pa}/V	E_{pc}/V	$I_P{}^b$/eV	Φ^c
P1	333, 372	347, 373	424	436	63	3.07	1.24	1.04	5.83	0.27
P2	391	402	437	452	50	2.75	0.75	0.59	5.20	0.89

[a] Determined from the onset position of the absorption band.
[b] Ionization potential (*vs.* vacuum) determined from onset of oxidation.
[c] Measured using quinine sulphate dihydrate as a standard.

other carbazole polymers which are protected with methyl-substituents at their 3,6-positions and which have absorption maxima at 317 and shoulder absorptions at 346 and 360 nm [9]. The size of the fluorine substituents at the 3,6-positions of the carbazole repeat units on polymer **P1** exerts less steric hindrance on the planarity of polymer chains than the methyl-substituents at the 3,6-positions in the methyl protected polymers.

The electronic spectra of polymer **P1** in the solid state display similar features to those in solutions with absorption maxima values at $\lambda_{max} = 347$ nm and 373 nm, indicating little structural differences between the polymer in solution and in the solid state. The optical band gap of polymer **P1** as determined from the onset of its absorption spectra in the solid state has a value $E_g = 3.07$ eV. This value is also an intermediate value between that of polymers with methyl-protecting groups ($E_g = 3.21$ eV) [9] and that without protecting groups at the 3,6-positions ($E_g \sim 2.9$ eV) [14] a further indication that **P1** has an intermediate electronic conjugation between the two sets of polymers.

The absorption spectra of copolymer **P2** are shown in Figure 2. The polymer displays an absorption band at $\lambda_{max} = 391$ nm in solution (toluene) and at $\lambda_{max} = 402$ nm in the solid state. The red shift in the absorption of copolymer **P2** when compared to that of polymer **P1** could be explained by the alternation of aryl amine donors and 3,6-difluoro-9-alkylcarbazole acceptor units on the copolymer chain leading to a relatively lower band gap polymer, estimated at

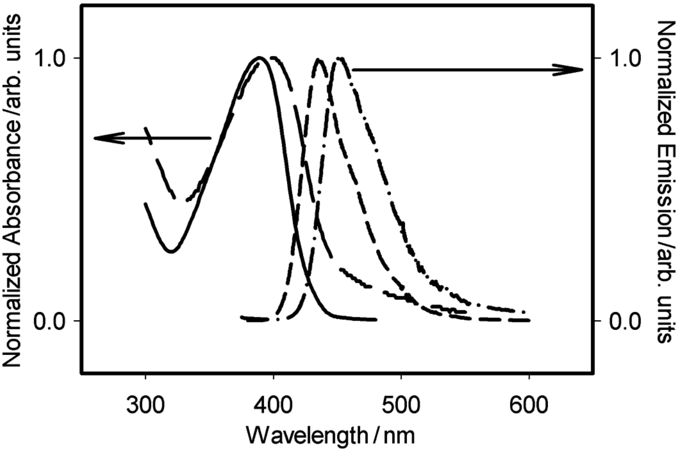


FIGURE 2 UV spectra of polymer **P2** in toluene (solid line), and as a film (long dashed line). PL spectra of **P1** in toluene (short dashed line) and as a film (dashed dot line).

$E_g = 2.75$ eV as determined from the onset of its absorption in the solid state. The close values of the absorption maxima of polymer **P2** in solution and in the solid state indicate little structural differences of the polymer in solution and in films.

Fluorescence studies on polymers **P1** and **P2** were performed in solution (toluene) and on films. The results of these studies are shown in Figures 1 and 2. Fluorescence spectra of polymer **P1** in solution showed an emission band at a λ_{max} value of 424 nm. It is interesting to note that while aryl functionalised polymer **P1** displays a band with no vibronic structure, the equivalent 9-alkyl functionalised polymer displays two emission bands at 418 and 441 nm [10]. The fluorescence spectrum of polymer **P1** in the solid state (Fig. 1) showed emission at 436 nm which are red-shifted with respect to those of the same polymer in toluene solutions. It also displays a relatively small Stokes shift (63 nm) pointing to small structural differences between its ground and excited states in the solid state. The measurement of the quantum yield of fluorescence of polymer **P1** in solution in toluene was also undertaken. This was determined on excitation of the polymer at its λ_{max} and comparison with the solution emission of quinine sulphate dihydrate ($\Phi_{fl} = 0.546$) used as a standard. The polymer displayed a quantum yield of fluorescence $\Phi = 0.27$. This value is lower than those observed for carbazole polymers with no protecting groups at the 3,6-positions which have fluorescence quantum yields between 0.59 and 0.76 [7], but it is similar to those observed for the equivalent polymers with methyl-substituents at the 3,6-positions which have fluorescence quantum yields between 0.16 and 0.25.

Fluorescence spectra of copolymer **P2** showed single emission bands at $\lambda_{max} = 437$ nm in solution (toluene) and at $\lambda_{max} = 452$ nm in the solid state. The emission of polymer **P2** in the solid state is slightly red shifted with respect to that of a similar alternating fluorene/triaryl amine copolymer (poly(9,9-dioctylfluorene-alt-N-(4-(3-methylpropyl))-diphenylamine), (**TFB**)) [15] which displays an emission at $\lambda_{max} = 431$ nm and a slightly wider band gap than polymer **P2** (2.75 eV for **P2** *vs*. 3.0 eV for **TFB**). Polymer **P2** displays a small Stokes shift (50 nm), indicating little structural differences between its ground and excited states. Measurement of the quantum yield of fluorescence of polymer **P2** in solution in toluene was also undertaken. The polymer displayed a high quantum yield of fluorescence $\Phi = 0.89$, a value much higher than that of homopolymer **P1**, indicating great promise for its application in light emitting diodes.

Electrochemical Studies: Cyclic voltammetry measurements on drop-cast polymer films were conducted in acetonitrile with tetrabutylammonium perchlorate as an electrolyte. The redox behaviour of polymer **P1** indicates a reversible redox wave with an oxidation wave at the potential $E_{pa} = 1.24\,V$ and an associated reduction wave at the potential E_{pc} at 1.04 V. The presence of fluorine substituents at the 3,6-positions of carbazole repeat units on **P1** results in the electrolytic stabilization of the polymer against degradation and side-reactions affecting the 3,6-positions when unprotected. In the same time it leads to a considerable increase of its ionization potential which increases from ~5.4 eV when no substituents are present at the 3,6-positions to 5.83 eV in the presence of fluorine as protecting groups in polymer **P1**. It must be noted that the ionization potential of **P1** is comparable to that of poly(9,9′-dialkylfluorene)s [16] (Ip ~5.8 eV) despite the fact that it has fluorine substituents on its repeat units. It has however, a slightly higher ionization potential than the equivalent 3,6-difluoro substituted 2,7-linked carbazole polymers with 9-alkyl substituents which have ionization potentials of about 5.7 eV [10]. The redox behaviour of polymer **P2** indicate a reversible redox wave with an oxidation wave at the potential $E_{pa} = 0.75\,V$ and an associated reduction wave at the potential E_{pc} at 0.59 V. The ionization potential of polymer **P2** as determined from the onset of its oxidation was found as $I_p = 5.20\,eV$. The presence of triaryl amine repeat units in polymer **P2** enables an easier hole injection into the polymer when compared to homopolymer **P1**. The ionization potential of polymer **P2** is similar to that reported for **TFB** which has an ionization potential $I_p = 5.33\,eV$ [17].

CONCLUSION

Fluoro-protected 2,7-linked 9-aryllcarbazole polymers and copolymers were prepared using respectively a one-pot modified Suzuki polycondensation synthetic route to prepare homopolymer **P1** and a conventional Suzuki polycondensation reaction to prepare copolymer **P2**. Both polymers emit in the blue part of the electromagnetic spectrum Fluorescence quantum yield measurements on the polymers in solution showed a quantum yield value of $\Phi = 0.27$ for polymer **P1** and a quantum yield value of $\Phi = 0.89$ for copolymer **P2**. Functionalisation of the 3,6-positions of carbazole repeat units with fluorine substituents imparts a good electrolytic stability to both polymers. It did however; increase the ionization potential of homopolymer **P1** to 5.83 eV as the result of the electron withdrawing effect of the fluorine substituents. Introduction of triaryl amine repeat units in copolymer **P2** allowed a substantial reduction of the ionization potential of the copolymer to 5.20 eV. All of the above physical properties of polymer **P2** indicate a great promise for its application in light emitting diodes. Investigations of the electroluminescent properties of both polymers are underway.

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