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Preparation and Properties of 4-Dialkylamino-phenyl *N*-Functionalized 2,7-Linked Carbazole Polymers

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The preparation of 2,7-linked carbazole polymers with 4-dialkylamino-phenyl substituents is presented. Poly(9-(4-dioctylamino-phenyl)-9*H*-carbazole-2,7-diyl) **P1** and poly(3,6-dimethyl-9-(4-dioctylamino-phenyl)-9*H*-carbazole-*alt*-9-(4-dioctylamino-phenyl)-9*H*-carbazole-2,7-diyl) **P2** were prepared through a Suzuki coupling polymerization route. The polymers were characterized by NMR spectroscopy, UV−vis absorption spectroscopy, and fluorescence spectroscopy and their molecular weights were estimated using gel permeation chromatography. Polymer **P1** had one of the highest average molecular weights reported for 2,7-linked carbazole main chain conjugated polymers. Both polymers showed unusual photophysical properties with solvent-dependent emission spectra. The fluorescence quantum yields of the polymers were also determined both in solution as well as in the solid state. Cyclic voltammetric studies on these polymers reveal reversible oxidation waves up to 0.7 V (vs Ag/Ag$^+$) for polymer **P1** and up to 1.0 V for polymer **P2**. The polymers also displayed low ionization potentials as a result of their *N*-substitution with the 4-dialkylamino-phenyl substituents.

Introduction

Recently, there has been significant interest in the development of wide band gap conjugated polymers for application in light-emitting diodes both as blue emitters as well as hosts for lower band gap fluorophores[1] and phosphorescent dyes.[2] 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. Application of poly(9,9′-dialkylfluorene)s in this area is, however, hampered by the luck of stability of blue light emission from devices made from this class of materials which has variously been assigned to excimer emission[3] arising from aggregates in films or formation of fluorenone repeat units as a result of oxidation[4] or both.[5] Furthermore, their high ionization potential—estimated at 5.8 eV[6] from electrochemical measurements—also results in a relatively large hole injection barrier from ITO ($\phi = 5.0$ eV). This thus requires the use of additional hole-transporting layers for efficient device performance. Introduction of aryl amines either as additional repeat units[7] along polymer chains or as pendent groups[8] has been shown as an efficient way to reduce the ionization potential of polyfluorenes as well as improve their hole-transport properties.

There is however growing interest in the development of alternative wide band gap conjugated polymers to polyfluorenes and we have shown recently[9] that poly(9-alkyl-9*H*-carbazole-2,7-diyl)s can be considered promising candidates for application in blue light emitting diodes in view of their high fluorescence quantum efficiencies and their lower ionizations potential (∼5.4 eV).

To produce 2,7-linked carbazole main chain conjugated polymers with even lower ionization potentials than those currently available (∼5.2−5.5 eV for poly(9-alkylcarbazole-2,7-diyl)s[10] and 5.8 eV for poly(9-arylcarbazole-2,7-diyl)s[11]), as well as with improved hole-transport properties, we have investigated the properties of 2,7-linked *N*-functionalized carbazole polymers with 4-dialkylamino-phenyl substituents. Our motivation for this comes from the fact that introducing electron-releasing 4-dialkylaminoaryl substituents

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at the 9-position on carbazole repeat units should in principle alter the electronic properties of these materials and may lead to carbazole polymers with improved electronic properties. In this work, we present our results on the preparation and properties of 2,7-linked *N*-functionalized carbazole polymers with 4-dialkylamino-phenyl substituents as well as that of analogous polymers where alternate carbazole repeat units are functionalized with methyl groups at the 3,6-positions.

Experimental Section

Materials. 2,7-Dibromo-3,6-dimethyl-9*H*-carbazole **1b**[10] and 2,7-dibromo-9-(4-amino-phenyl)-9*H*-carbazole **3a**[12] were obtained according to literature procedures. Tetrahydrofuran (THF) was distilled over sodium-benzophenone under an inert nitrogen atmosphere. 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 and 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 analyzed neat, using NaCl-plate method and solid samples were analyzed using the Diamond ATR attachment for solid samples. Melting points were obtained using a Gallenkamp Melting Point Apparatus. GC-MS spectra were recorded on a Perkin-Elmer Turbomass Mass Spectrometer equipped with a 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 a Waters Model 515 HPLC Pump, GILSON Model 234 Autoinjector, MILLIPORE Waters Lambda-Max Model 481 LC Spectrometer, Erma ERC-7512 RI Detector, PLgel 5m 500A Column, and PLgel 10m 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 an Hitachi U-2010 Double Beam UV/Visible Spectrophotometer. The absorbance of polymers was measured in solution in spectrophotometric-grade solvents (dichloromethane, tetrahydrofuran, and 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 an Hitachi F-4500 Fluorescence Spectrophotometer equipped with an 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 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 solvents (dichloromethane, tetrahydrofuran, and toluene) at 25 °C. The oxygen quenching effects on polymers **P1** and **P2** were examined by comparing the photoluminescence spectra of their solution in the air with those under an argon atmosphere. Since the solutions exhibited no oxygen quenching effect, photoluminescence spectra measurements of their solutions were carried out in the air. 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. The correction factors were obtained by excitation spectra measurement of the quantum counter (Rhodamine B standard solution) for the excitation side and by synchronous wavelength scan using a light diffuser for the emission side. The light diffuser (parts No. 650-1576) was provided with the spectrophotometer as an accessory. The correction factors obtained were stored in the memory of the spectrophotometer. As a result, the spectrophotometer automatically gave corrected excitation and emission spectra when measurements were carried out.

Harmine and quinine sulfate dihydrate in 0.05 mol dm^{-3} (0.5 mol dm^{-3} for quinine sulfate dihydrate) sulfuric acid were employed as fluorescence standards. The quantum yields in diluted solutions were obtained by comparison with a fluorescence standard of a known quantum yield using the following equation,

$$\Phi_x = \Phi_s \times (S_s/A_s)^{-1} \times (S_x/A_x) \times (n_x^{\,2}/n_s^{\,2})$$

where the subscripts "s" and "x" refer to the standard and the unknown sample solutions, Φ is the quantum yield, *A* is the absorbance at the excitation wavelength, *S* is the integral intensity of the corrected photoluminescence spectra, and *n* is the refractive index of the solvent. The fluorescence standard solution and the unknown sample solution were excited at the same wavelength. Quinine sulfate dihydrate solution in 0.5 mol dm^{-3} sulfuric acid ($\Phi_s = 0.546$) was employed as the fluorescence standard solution. The refractive indexes of the solvents were taken as 1.339, 1.334, and 1.4961 respectively for 0.5 mol dm^{-3} sulfuric acid, 0.05 mol dm^{-3} sulfuric acid, and toluene. (S/A) values of each sample in solution could simply be obtained by dividing the integral intensities of the spectra by the absorbances at the excitation wavelengths using a sample solution of a certain concentration. To minimize experimental error, the final (S/A) values used in the calculations for each sample were obtained from the plots of the integral intensities of the spectra vs the absorbances at the excitation wavelengths using sample solutions of various concentrations. The reliability of our measurements was confirmed upon measurement of the quantum yield of harmine using quinine sulfate dihydrate as a standard. The experimental value obtained was identical to that reported in the literature ($\Phi_s = 0.45$).[13] Solid-state quantum yield measurements were carried out on spin-cast thin films of **P1** and **P2**. The polymers were dissolved in toluene at a concentration of 20 mg cm^{-3} and the films were spin-cast onto quartz substrates at 1000 rpm. The samples were mounted inside a LabSpec integrating sphere and excited using the 351 and 364 nm lines of an argon ion laser. To minimize the occurrence of photo-oxidation, the laser was attenuated and defocused to an approximate power density of 1 mW cm^{-2} and the sphere was flushed with nitrogen. Light from within the

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sphere was collected via an optical fiber and detected using a scanning monochromator and photomultiplier tube. The spectral response of the combined sphere-fiber detector system was determined by measuring the emission from a tungsten halogen lamp that had been supplied and calibrated by the National Physical Laboratory. The quantum yield was calculated by measuring the relative number of photons emitted by the polymer compared to the relative number of photons absorbed. This technique was described previously[1] and is based upon the methodology of de Mello et al.[14] We have confirmed the calibration of our sphere system by measuring the quantum efficiency of thin films of a well-characterized conjugated polymer poly(9,9′-dioctyl fluorene) [F8] supplied by the Dow Chemical Company. Here, we recorded a quantum efficiency of 0.46 ± 0.05, a value in excellent agreement with previous literature reports.[15]

Cyclic voltammograms were recorded using a Princeton Applied Research Model 263A Potentiostat/Galvanostat. Measurements were carried out under argon at 25 ± 2 °C. Tetrabutylammonium perchlorate (TBAClO$_4$) (10 cm^3) 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 × 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 and then dried in air. Ferrocene was employed as a reference redox system according to IUPAC's recommendation.[16]

All reactions were carried out under an inert nitrogen atmosphere.

Preparation of Monomers. *2,7-Dibromo-3,6-dimethyl-9-(4-nitro-phenyl)-9H-carbazole **2b**.* A mixture of 2,7-dibromo-3,6-dimethyl-9*H*-carbazole **1b** (4.50 g, 12.70 mmol), anhydrous potassium carbonate K$_2$CO$_3$ (8.85 g, 64.00 mmol), 4-fluoronitrobenzene (6.38 g, 45.20 mmol), and DMF (60 cm^3) was heated at reflux in DMF for 24 h. Once cooled to room temperature, it was poured into warm (40 °C) water (500 cm^3). The yellow solid was collected by filtration and the crude material was washed with several portions of warm water (40 °C) and then recrystallized from toluene and then from chloroform to afford the product as bright yellow crystals (4.23 g, 70.0% yield). mp 303−305 °C. Mass (EI) (*m*/*z*): 472, 474, 476 (M$^{•+}$). IR (KBr): 3050−2900, 1588.0, 1509.9, 1497.6, 1465.6, 1445.9, 1374.1, 1356.0, 1331.3, 1303.3, 1230.5, 1135.1, 1102.6, 1038.5, 998.4, 970.9, 950.8, 879.8, 863.0, 838.1, 749.3, 711.5, 693.2, 672.4, 633.8, 613.1 cm^{-1}. ^{1}H NMR (CDCl$_3$, TMS) δ_H/ppm: 8.50 (2H, m), 7.91 (2H, s), 7.73 (2H, m), 7.63 (2H, s), 2.56 (6H, s). ^{13}C NMR (CDCl$_3$) δ_C/ppm: 146.13, 143.08, 139.27, 130.69, 126.53, 125.86, 123.19, 122.96, 121.75, 113.39, 23.14. Anal. Calcd for C$_{20}$H$_{14}$Br$_2$N$_2$O$_2$: C, 50.66; H, 2.98; Br, 33.70; N, 5.91. Found: C, 50.57; H, 2.93; Br, 33.73; N, 5.84.

*2,7-Dibromo-3,6-dimethyl-9-(4-amino-phenyl)-9H-carbazole **3b**.* A mixture of 2,7-dibromo-3,6-dimethyl-9-(4-nitro-phenyl)-9*H*-carbazole **2b** (4.01 g, 8.46 mmol), SnCl$_2$•2H$_2$O (10.65 g, 47.20 mmol), and ethanol (140 cm^3) was heated at reflux for 24 h and then cooled to room temperature. The ethanol was removed in vacuo and the resulting residue washed with a 10% (w/w) aqueous solution of sodium hydroxide (300 cm^3). The organic material was extracted with diethyl ether. The organic solution was then dried with MgSO$_4$, filtered, and evaporated to dryness in vacuo. The resulting solid was purified via column chromatography (silica gel, petroleum ether/ethyl acetate/triethylamine 5/2/0.8 (v/v/v) to give ivory crystals of 2,7-dibromo-3,6-dimethyl-9-(4-amino-phenyl)-9*H*-carbazole **3b** (3.46 g, 92.1% yield). mp 170−172 °C. Mass (EI) (*m*/*z*): 442, 444, 446 (M$^{•+}$). IR (KBr): 3400, 3050−2900, 1616.3, 1601.8, 1516.5, 1450.8, 1362.5, 1304.1, 1287.9, 1252.2, 1237.0, 1179.7, 1124.0, 1039.6, 997.5, 953.9, 935.3, 859.6, 832.0, 794.3, 717.9, 671.0, 643.7, 631.5, 615.9 cm^{-1}. ^{1}H NMR (CDCl$_3$, TMS) δ_H/ppm: 7.82 (2H, s), 7.39 (2H, s), 7.14 (2H, m), 6.78 (2H, m), 3.82 (2H, br.s), 2.48 (6H, s). ^{13}C NMR (CDCl$_3$) δ_C/ppm: 146.37, 140.99, 128.57, 128.24, 127.21, 122.60, 121.78, 121.35, 116.00, 113.42, 23.14. Anal. Calcd for C$_{20}$H$_{16}$Br$_2$N$_2$: C, 54.08; H, 3.63; Br, 35.98; N, 6.31. Found: C, 54.07; H, 3.69; Br, 36.11; N, 6.29.

*2,7-Dibromo-9-(4-dioctylamino-phenyl)-9H-carbazole **4a**.* 2,7-Dibromo-9-(4-amino-phenyl)-9*H*-carbazole **3a** (4.85 g, 11.7 mmol), 1-iodooctane (13.30 g, 55.39 mmol), anhydrous K$_2$CO$_3$ (8.0 g, 57.88 mmol), and butan-1-ol (80 cm^3) were placed in a flask and degassed under high vacuum for 5 min and the mixture was refluxed for 48 h under an inert atmosphere. The reaction mixture was then cooled to room temperature and additional portions of 1-iodooctane (7.98 g, 33.19 mmol) and K$_2$CO$_3$ (4.80 g, 34.73 mmol) were added. The mixture was refluxed for a further 24 h. The mixture was again cooled to room temperature and water (200 cm^3) was added. The mixture was extracted with dichloromethane (3 × 200 cm^3) and the combined organic phases were washed with water (200 cm^3) and dried over magnesium sulfate. The solvent and side product (1-butoxy-octane) were removed by heating the mixture (50−55 °C) under high vacuum to leave a residue which was purified by column chromatography on silica gel 60 using first petroleum ether as eluent and then a solvent combination of petroleum ether/triethylamine/ethyl acetate (20:1:1) (v/v/v), to afford 2,7-dibromo-9-(4-dioctylamino-phenyl)-9*H*-carbazole **4a**, as a white solid (6.43 g, 86% yield). mp: 58−59 °C. Mass (EI) (*m*/*z*): 638, 640, 642 (M$^{•+}$). ^{1}H NMR (CDCl$_3$, TMS) δ_H/ppm: 7.89 (2H, d, J = 8 Hz), 7.43 (2H, d, J = 2 Hz), 7.33 (2H, dd, J = 8 Hz, J = 2 Hz), 7.24 (2H, d, J = 8 Hz), 6.76 (2H, d, J = 8 Hz), 3.33 (4H, t, J = 8 Hz), 1.65 (4H, m), 1.12−1.46 (20H, m), 0.80−0.95 (6H, m). ^{13}C NMR (CDCl$_3$) δ_C/ppm: 148.05, 142.74, 128.20, 123.17, 122.95, 121.28, 119.74, 113.20, 112.12, 51.25, 31.86, 29.53, 29.37, 27.23, 22.68, 14.13. Anal. Calcd for C$_{34}$H$_{44}$Br$_2$N$_2$: C, 63.75; H, 6.92; N, 4.37; Br, 24.95. Found: C, 63.87; H, 6.75; N, 4.48; Br, 24.88.

*2,7-Dibromo-3,6-dimethyl-9-(4-dioctylamino-phenyl)-9H-carbazole **4b**.* 2,7-Dibromo-3,6-dimethyl-9-(4-amino-phenyl)-9*H*-carbazole **3b** (1.10 g, 2.48 mmol), 1-iodooctane (6.4 g, 27 mmol), and anhydrous K$_2$CO$_3$ (2.15 g, 15.60 mmol) were refluxed in 1-butanol (100 cm^3) under an inert atmosphere. The reaction was monitored daily by TLC (petroleum ether/ethyl acetate, 25/1 (v/v) R_f (starting material) = 0.05, R_f (mono-alkylated product) = 0.33, R_f (bis-alkylated product) = 0.67); if the presence of starting material and/or mono-alkylated product was detected, the reaction was cooled to room temperature and an additional portion of anhydrous potassium carbonate (1.0 g, 7.50 mmol) and 1-iodooctane (2.7 g, 11.00 mmol) were added. The reaction was run at reflux for 5 days, with four extra portions of potassium carbonate and 1-iodooctane being added. Once the reaction was complete, the 1-butanol and other side products were removed via vacuum distillation. The residue was then extracted with dichloromethane and washed with distilled water. The organic solution was dried over MgSO$_4$, filtered, and reduced in vacuo. The product was then purified via flash column chromatography (silica gel, petroleum ether/triethylamine, 20/1 (v/v) (once impurities were collected from the column, product was eluted with ethyl acetate). The solvents were removed from the product in vacuo to give a viscous oil of 2,7-dibromo-3,6-dimethyl-9-(4-dioctylamino-phenyl)-9*H*-carbazole **4b** (0.60 g, 36.2%

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yield). TLC (petroleum ether/triethylamine, 25:1 (v/v), $R_f = 0.42$). Mass (EI) (m/z): 666, 668, 670 ($M^{\bullet+}$). IR (KBr): 2925.1, 2854.1, 1602.3, 1521.6, 1459.0, 1401.8, 1359.2, 1303.3, 1256.4, 1237.9, 1188.9, 1167.4, 111.8, 1040.1, 996.7, 958.4, 865.8, 848.6, 816.9, 719.7, 617.4 cm^{-1}. ^1H NMR ($CDCl_3$, TMS) δ_H/ppm: 7.89 (2H, s), 7.50 (2H, s), 7.22 (2H, d, $J = 9$ Hz), 6.75 (2H, d, $J = 9$ Hz), 3.33 (4H, t, $J = 7$ Hz), 2.55 (6H, s), 1.66 (4H, br. s), 1.33 (20H, m), 0.89 (6H, m). ^{13}C NMR ($CDCl_3$) δ_C/ppm: 147.78, 141.22, 128.32, 128.07, 123.82, 122.52, 121.69, 121.25, 113.55, 112.09, 51.27, 46.19, 31.89, 29.57, 29.41, 27.27, 23.09, 22.72, 14.17. Anal. Calcd for $C_{36}H_{48}Br_2N_2$: C, 64.67; H, 7.24; Br, 23.90; N, 4.19. Found: C, 64.75; H, 7.30; Br, 23.88; N, 3.90.

2,7-Bis(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)- 9-(4-dioctylamino-phenyl)-9H-carbazole ***5a***. *tert*-Butyllithium (11 cm^3, 18.75 mmol, 1.7 M in pentane) was added dropwise over 15 min to a solution of 2,7-dibromo-9-(4-dioctylamino-phenyl)-9*H*-carbazole **4a** (4 g, 6.25 mmol) in THF (200 cm^3) at −78 °C. The reaction mixture was stirred at −78 °C for 4 h. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11.86 g, 63.74 mmol) was then added dropwise to the solution at −78 °C and the reaction mixture was stirred at −78 °C for a further 2 h. The reaction mixture was then allowed to warm up to ambient temperature and stirred for another 36 h. The reaction mixture was then poured onto water (250 cm^3) and extracted with diethyl ether (3 × 200 cm^3). The organic extracts were combined and washed with water and dried over $MgSO_4$ and the solvent was removed in vacuo. Addition of petroleum ether to the crude product (300 cm^3) produced a precipitate that was filtered to afford pure product **5a** as a white solid (4.2 g, 91.5% yield). mp 190−191 °C. ^1H NMR ($CDCl_3$, TMS) δ_H/ppm: 8.15 (2H, d, $J = 8$ Hz), 7.78 (2H, s), 7.71 (2H, d, $J = 8$ Hz), 7.30 (2H, d, $J = 8$ Hz), 6.78 (2H, d, $J = 8$ Hz), 3.35 (4H, t, $J = 8$ Hz), 1.70 (4H, m), 1.10−1.43 (44H, m), 0.79−0.93 (6H, m). ^{13}C NMR ($CDCl_3$) δ_C/ppm: 147.70, 141.90, 128.85, 125.47, 125.10, 124.81, 119.75, 116.49, 112.20, 83.69, 51.31, 31.87, 29.55, 29.37, 29.07, 27.39, 27.28, 24.87, 22.68, 14.13. Anal. Calcd for $C_{46}H_{68}B_2N_2O_4$: C, 75.20; H, 9.33; N, 3.81. Found: C, 75.11; H, 9.48; N, 3.80.

Preparation of Polymers. *Poly(9-(4-dioctylamino-phenyl)-9H-carbazole-2,7-diyl)* ***P1***. THF (10 cm^3) was added to a mixture of tris(dibenzylideneacetone) dipalladium ($Pd_2(dba)_3$) (0.005 g, 0.0055 mmol) and triphenylphosphine (0.012 g, 0.046 mmol) and the vessel heated to 60 °C for 30 min under an inert atmosphere. The solution was then cooled to room temperature. A second solution comprising 2,7-dibromo-9-(4-dioctylamino-phenyl)-9*H*-carbazole **4a** (0.448 g, 0.70 mmol) and 2,7-bis(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)-9-(4-dioctylamino-phenyl)-9 *H*-carbazole **5a** (0.514 g, 0.70 mmol) in THF (15 cm^3) was prepared and added to the first solution at room temperature, followed by addition of $NaHCO_3$ (1.00 g, 11.90 mmol) and de-oxygenated water (10 cm^3). The reaction mixture was then heated to reflux for 24 h. The mixture was cooled to room temperature and THF (120 cm^3) was added to dissolve insoluble polymeric materials, followed by addition of bromobenzene (0.15 g, 0.95 mmol) at room temperature and refluxing of the solution for 1 h. The solution was cooled to room temperature, phenylboronic acid (0.12 g, 0.99 mmol) was added, and the mixture was refluxed for an additional 1 h and then cooled to room temperature. The mixture was then poured into chloroform (300 cm^3) and the organic layer washed with water (200 cm^3) and dried over $MgSO_4$. The solution was concentrated to a volume of ~20 cm^3 and then added to methanol (500 cm^3) to precipitate the polymer which was collected by filtration. The polymer was further reprecipitated from chloroform/methanol twice to afford **P1**, as a light yellow powder (0.63 g, 94% yield). GPC: $M_w = 87600$; $M_n = 17400$; $M_w/M_n = 5.0$. ^1H NMR ($CDCl_3$, TMS) δ_H/ppm: 8.15 (2H, d, $J = 8$ Hz), 7.60 (2H, s), 7.50 (2H, d, $J = 8$ Hz), 7.36 (2H, d, $J = 8$ Hz), 6.80 (2H, d, $J = 8$ Hz), 3.35 (4H, m), 1.70 (4H, m), 1.20−1.43 (20H, m), 0.80−0.95 (6H, m). ^{13}C NMR ($CDCl_3$) δ_C/ppm: 147.62, 142.75, 140.32, 128.43, 124.82, 121.82, 120.11, 119.82, 112.16, 109.02, 51.28, 31.84, 29.52, 29.37, 27.35, 27.26, 22.66, 14.10. Anal. Calcd for $C_{34}H_{44}N_2$: C, 84.87; H, 9.15; N, 5.82. Found: C, 84.16; H, 8.66; N, 5.43; Br, 0.00.

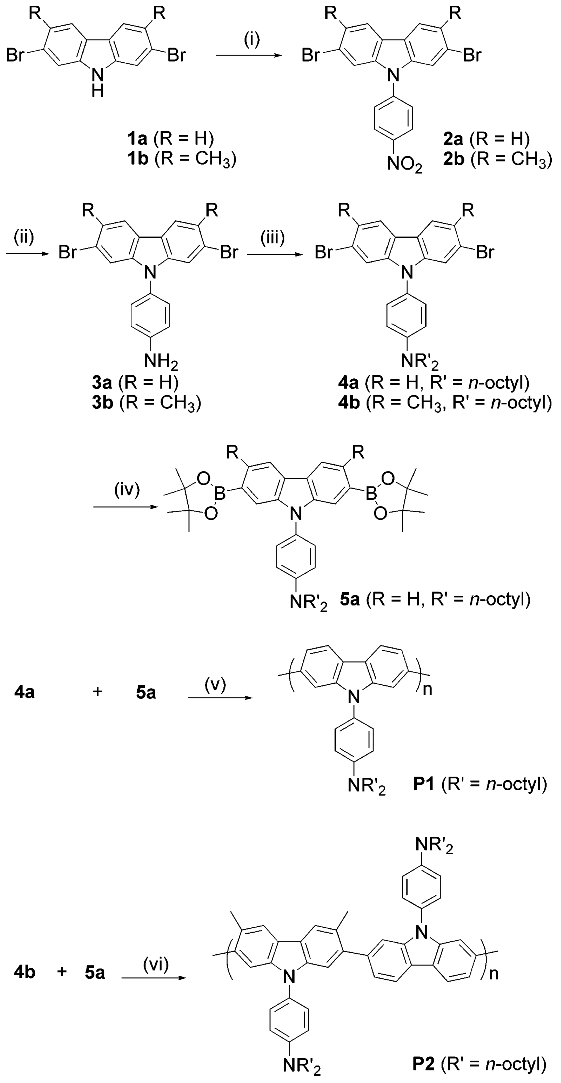
A portion of polymer **P1** was fractionated according to the following procedure: 0.45 g of the polymer was dissolved in THF (200 cm^3), methanol (60 cm^3) was added dropwise, and part of the polymer came out of solution. The mixture was stirred for 1 h and then heated up to reflux under nitrogen until the polymer dissolved again. It was cooled down to room temperature while stirring overnight. The resulting precipitate was collected by filtration to afford polymer **P1** as a light yellow fibrous solid (0.31 g, 69% yield). GPC: $M_w = 148800$; $M_n = 93000$; $M_w/M_n = 1.6$.

Poly(3,6-dimethyl-9-(4-dioctylamino-phenyl)-9H-carbazole-2,7-diyl-alt-9-(4-dioctylamino-phenyl)-9H-carbazole-2,7-diyl) ***P2***. Pd_2-$(dba)_3$ (0.005 g, 0.0055 mmol) and triphenylphosphine (0.012 g, 0.046 mmol) were heated while stirring to 60 °C in dry tetrahydrofuran (10 cm^3) under an inert N_2 atmosphere for 30 min. The solution was then cooled to room temperature and a solution of 2,7-dibromo-3,6-dimethyl-9-(4-dioctylamino-phenyl)-9*H*-carbazole **4b** (0.504 g, 0.753 mmol) and 2,7-bis-(4,4,5,5-tetramethyl-[1,3,2]dioxaborolan-2-yl)- 9-(4-dioctylamino-phenyl)-9*H*-carbazole **5a** (0.553 g, 0.753 mmol) in dry tetrahydrofuran (15 cm^3) was added. The system was then placed under N_2 and stirred for 5 min. A solution of $NaHCO_3$ (1.00 g, 11.90 mmol) in 10 cm^3 of distilled H_2O was added and the mixture placed under an inert atmosphere again and heated to reflux for 45 h. The reaction was then cooled to room temperature and a solution of $Pd(PPh_3)_4$ (0.007 g, 0.006 mmol) in THF (10 cm^3) was added, followed by addition of bromobenzene (0.15 g, 0.95 mmol), and the mixture was refluxed for 1 h. The solution was again cooled to room temperature, phenylboronic acid (0.12 g, 0.99 mmol) added, and the mixture refluxed for a further 1 h and then cooled to room temperature. The mixture was then poured into chloroform (300 cm^3) and the organic layer washed with water (200 cm^3) and then dried over $MgSO_4$. The solution was concentrated to a volume of ~20 cm^3 and then added to methanol (500 cm^3) to precipitate the polymer which was collected by filtration. The polymer was further reprecipitated from chloroform/methanol twice to afford **P2**, as a creamy white powder (0.585 g, 78.5% yield). GPC: $M_w = 7500$, $M_n = 3000$, $M_w/M_n = 2.4$. ^1H NMR ($CDCl_3$, TMS) δ_H/ppm: 8.07 (2H, d, $J = 7$ Hz), 7.91 (2H, s), 7.30 (10 H, br m), 6.61 (4H, br m), 3.20 (8H, m), 2.35 (6H, br s), 1.49 (8H, m), 1.19 (40H, m), 0.78 (12H, m). IR (ν/cm^{-1}): 2923.0, 2851.7, 1604.0, 1518.1, 1454.2, 1400.1, 1358.1, 1326.4, 1231.1, 1190.0, 1165.0, 1145.3, 1109.6, 990.6, 938.4, 912.6, 866.0, 811.4, 767.4, 720.3, 644.4, 620.0, 608.6. Anal. Calcd for $C_{70}H_{92}N_4$: C, 84.97%; H, 9.37%; N, 5.66%. Found: C, 83.09%; H, 8.99%; N, 5.32%; Br, 0.00.

Results and Discussion

Synthesis and Characterization of the Polymers. The preparation of polymers **P1** and **P2** is outlined in Scheme 1. The synthesis starts by the preparation of the known intermediate 2,7-dibromo-9-(4-amino-phenyl)-9*H*-carbazole **3a** according to literature procedures.[12] The preparation of new intermediate 2,7-dibromo-3,6-dimethyl-9-(4-amino-phenyl)-9*H*-carbazole **3b** was undertaken using similar experimental procedures upon reaction of carbazole **1b** with 4-fluoronitrobenzene in the presence of a base to obtain 2,7-dibromo-3,6-dimethyl-9-(4-nitro-phenyl)-9*H*-carbazole **2b**,

Scheme 1[a]



(i) $F{-}C_6H_4{-}NO_2$, K_2CO_3, DMF, reflux; (ii) $SnCl_2{\cdot}2H_2O$, EtOH, reflux; (iii) 1-iodooctane, K_2CO_3, 1-butanol, reflux; (iv) (a) *tert*-butyllithium, THF, −78 °C; (b) 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane; (v) (a) $Pd_2(dba)_3/PPh_3$ (1/8), $NaHCO_3$, THF/H_2O; (b) PhBr; (c) $PhB(OH)_2$; (vi) (a) $Pd_2(dba)_3/PPh_3$ (1/8), $NaHCO_3$,THF/H_2O; (b) $Pd(PPh_3)_4$; (c) PhBr; (d) $PhB(OH)_2$.

followed by its reduction with tin(II) chloride to afford **3b** in good yields. Monomer **4a** was obtained upon bis-alkylation of amine **3a** upon its reaction with 1-iodooctane in the presence of potassium carbonate in refluxing 1-butanol. The reaction was accompanied by the formation of 1-butoxy-octane as a side product. Monitoring the reaction mixture by thin layer chromatography and further additions of 1-iodooctane and potassium carbonate did, however, allow the preparation of **4a** in good yields (86%). Bis-alkylation of **3b** to afford **4b** proved more difficult under these conditions and the product was produced in modest yields (36%). It is worth noting that the use of dimethylformamide, dimethyl sulfoxide, or 5-methyl-2-pyrrolidinone at high temperature as a solvent for the reaction, instead of 1-butanol, was always accompanied by the formation of degradation products. The bis-boronic ester derivative **5a** was prepared in good yield upon lithium-halogen exchange of dibromide **4a** on reaction with *tert*-butyl lithium at low temperature, followed by quenching with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. Polymers **P1** and **P2** were obtained in good yields upon reaction of the bis-boronic ester derivative **5a** with respectively dibromides **4a** and **4b** using a Suzuki-type cross-coupling condensation polymerization reaction (Scheme 1). The polymerization reactions were carried out using $Pd_2(dba)_3$ and triphenylphosphine as precursor catalysts at a ratio of 1:8 and sodium hydrogen carbonate as a base in tetrahydrofuran/water at reflux temperatures.

Gel permeation chromatography results from these polymerization reactions (using polystyrene standards) have shown average molecular weight values M_w of 87600 Da with a polydispersity value of 5 for polymer **P1**. Fractionation of polymer **P1** upon its precipitation from tetrahydrofuran solutions with methanol afforded polymer fractions with high average molecular weight values (M_w of 148800 Da) and narrower polydispersities (1.6) corresponding to degrees of polymerization of ∼190 which are among the highest values described for these classes of 2,7-linked carbazole main chain conjugated polymers described in the literature. An average molecular weight M_w of 7500 Da with a polydispersity value of 2.4 was obtained for polymer **P2**. It is clear that, under the same polymerization conditions, the degree of polymerization of polymer **P2** is lower than that of polymer **P1**, most likely as a consequence of the steric effects of the methyl substituents at the 3,6-positions on monomer **4b**, which impede the polymerization reaction.

NMR Spectroscopy. NMR studies were conducted in chloroform, on the resulting carbazole polymers. ^1H NMR studies on poly(9-(4-dioctylamino-phenyl)-9*H*-carbazole-2,7-diyl) **P1** reveal in the aromatic region a doublet at 8.15 ppm corresponding to the hydrogens at the 4- and 5-positions of carbazole rings, a singlet at 7.60 ppm corresponding to the hydrogens at the 1- and 8-positions, a doublet at 7.50 ppm corresponding to the two hydrogens on the benzene ring on the carbons ortho to the carbazole nitrogen atom, a doublet at 7.36 ppm corresponding to hydrogens at the 3- and 6-positions, and another doublet at 6.80 ppm corresponding to the two hydrogens on the benzene ring on the carbons meta to the carbazole nitrogen atom. In addition, a broad multiplet centered around 3.35 ppm, corresponding to hydrogens of the methylene groups directly attached to the nitrogen atom on the para position of the benzene ring attached at the 9-position of the carbazole rings could also be seen along with the rest of the hydrogens of the octyl-group substituents. ^{13}C NMR studies on polymer **P1** reveal in the aromatic region ten chemical environments at around 147.62, 142.75, 140.32, 128.43, 124.82, 121.82, 120.11, 119.82, 112.16, and 109.02 ppm, corresponding respectively to the carbon linked to the dioctylamino groups, carbons at the 8a- and 9a-positions of carbazole rings, the benzene carbon attached to the 9-position of carbazole rings, carbons at the 2- and 7-positions of carbazole rings, carbons on the ortho positions to the benzene carbon attached to the 9-position of carbazole rings, carbons at the 4- and 5-positions of carbazole rings, carbons at the 3- and 6-positions of carbazole rings, carbons at the 4a- and 4b-positions of carbazole rings, carbons on the meta positions to the benzene carbon attached to the 9-position of carbazole rings, and

Table 1. UV−Vis and Fluorescence Data of Polymers P1 and P2

	absorption		emission				
polymer	λ_{max}/nm (CH_2Cl_2)	λ_{max}/nm (film)	λ_{max}/nm (toluene)	$\lambda_{max}{}^{a}$/nm (film)	Φ^{b} (toluene)	Stokes shift/nm	band gap^{c}/eV
P1	273, 382	274, 388	417 (441)	422 (448)	0.53	34	2.89
P2	271, 332	314, 352	434	436 (502)	0.14	84	3.05

[a] Numbers in brackets correspond to shoulder emission peaks. [b] Measured using quinine sulfate dihydrate as a standard. [c] Determined from the onset position of the absorption band.

carbons at the 1- and 8-positions of carbazole rings. These NMR results indicate a homogeneous structure for the poly-(9-(4-dioctylamino-phenyl)-9*H*-carbazole-2,7-diyl) **P1** prepared in this study with exclusive 2,7-linkage of carbazole repeat units on polymer chains.

^{1}H NMR studies on poly(3,6-dimethyl-9-(4-dioctylamino-phenyl)-9*H*-carbazole-*alt*-9-(4-dioctylamino-phenyl)-9*H*-carbazole-2,7-diyl) **P2** were also in agreement with the assigned structure and revealed a broad doublet and a broad singlet at 8.07 and 7.91 ppm assigned respectively to the hydrogens at the 4- and 5-positions and hydrogens at the 1- and 8-positions of non-methylated carbazole rings, a broad multiplet at 7.30 ppm assigned to the hydrogens on the benzene rings on the carbons ortho to the carbazole nitrogen atoms, as well as hydrogens at the 3- and 6-positions of non-methylated carbazole rings and those at the 1- and 8-positions and 4- and 5-positions of methylated carbazole repeat units. Another multiplet at 6.61 ppm corresponding to the hydrogens on the benzene rings on the carbons meta to the carbazole nitrogen atoms is also identified. In addition, a broad multiplet centered around 3.20 ppm, corresponding to hydrogens of the methylene groups directly attached to the nitrogen atom on the para position of the benzene rings attached at the 9-position of the carbazole rings could also be seen along with the signals from the methyl groups attached to alternate carbazole rings at 2.35 ppm and the rest of the hydrogens of the octyl-group substituents. These NMR results indicate a homogeneous structure for the poly-(3,6-dimethyl-9-(4-dioctylamino-phenyl)-9*H*-carbazole-*alt*-9-(4-dioctylamino-phenyl)-9*H*-carbazole-2,7-diyl) **P2** prepared in this study with exclusive 2,7-linkage of carbazole repeat units on polymer chains.

Solution and Solid-State Electronic Spectra. The extent of π orbital overlap between neighboring repeat units on polymers **P1** and **P2** can be directly assessed from their electronic spectra. Table 1 shows the absorption maxima values, for the carbazole polymers both in solution and in the solid state (films). Polymer **P1** displays a maximum absorption in solution (dichloromethane) at a λ_{max} value of 382 nm. This value is similar to those reported for poly(9-alkyl-9*H*-carbazole-2,7-diyl)[9] (Figure 1), indicating similar degrees of electronic conjugation in the two classes of materials. The electronic spectra of the polymer in the solid state display similar features to those in solution with very close absorption maxima values ($\lambda_{max} = 388$ nm). 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 2.89 eV which was also similar to those of poly(9-alkyl-9*H*-carbazole-2,7-diyl).[9]

Polymer **P2** displays a maximum absorption in solution (dichloromethane) at a λ_{max} value of 332 nm. The electronic spectrum of the polymer in the solid state displays a red shift with a λ_{max} value at 352 nm, indicating a greater electronic conjugation in films (Figure 2). The band gap of polymers **P2** as determined from the onset position of its absorption band E_g is around 3.05 eV. It is clear from these data that the presence of methyl substituents at the 3,6-positions on alternate carbazole repeat units in these polymers is clearly reducing the planarity of the polymer backbones and leading to lower absorption wavelengths both in solutions and films and higher band gaps.

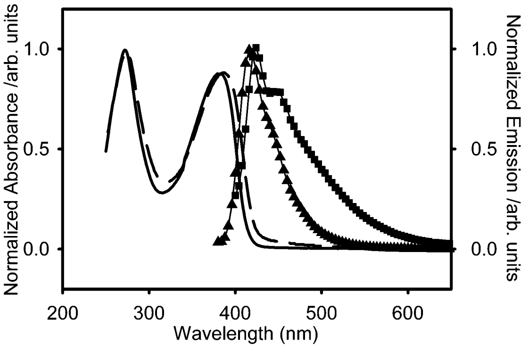


Figure 1. UV spectra of **P1** in dichloromethane (solid line) and as a film (dashed line). PL spectra of **P1** in toluene (triangles) and as a film (squares).

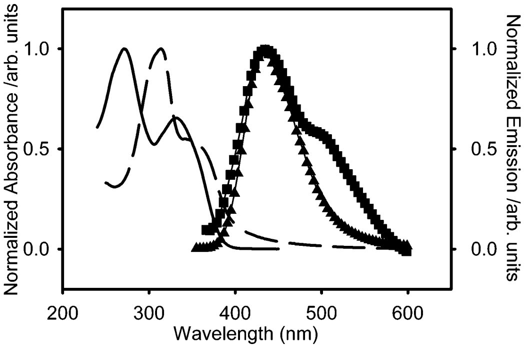


Figure 2. Absorbance spectra of **P2** in toluene (solid line) and as a film (dashed line). PL spectra of **P2** in toluene (triangles) and as a film (squares).

Solution and Solid-State Fluorescence Spectra. Fluorescence studies on polymers **P1** and **P2** were performed both in solution in toluene and in the solid state. Results of the studies undertaken in solution in toluene and as films are shown in Table 1. The spectra are also included in Figures 1 and 2. Polymer **P1** showed emission bands at a λ_{max} value of 417 nm with a shoulder peak at 441 nm. Its fluorescence spectrum as a film displays an emission band at 422 nm together with a shoulder at 448 nm. These emission spectra are very much comparable to those of poly(9-alkyl-*9H*-carbazole-2,7-diyl)[9] in studies undertaken in dichloromethane and in films. Data in Table 1 on polymer **P1** also indicate a small Stokes shift, indicating small structural differences between the ground and excited states in this polymer.

Table 2. Comparison of Fluorescence Data of Polymers P1 and P2 in Different Solvents and as Films

	emission			
polymer	λ_{max}/nm (toluene)	$\lambda_{max}{}^{a}$/nm (THF)	$\lambda_{max}{}^{a}$/nm (CH_2Cl_2)	$\lambda_{max}{}^{a}$/nm (film)
P1	417 (441)	418, 473	417, 486	422 (448)
P2	434	465	473	436 (502)

[a] Numbers in brackets correspond to shoulder emission peaks.

Polymer **P2** showed a broad emission band at a λ_{max} value of 434 nm in solution in toluene. Its fluorescence spectrum as a film displays an emission band at 436 nm together with a shoulder at 502 nm. It is not immediately obvious why the emission bands of polymer **P2** are red-shifted when compared to those of polymer **P1** given that polymer **P2** has a slightly larger band gap than polymer **P1**. However, it is clear from that the Stokes shift for polymer **P2** is much larger (84 nm vs 34 nm for **P1**), indicating large structural differences between the ground and excited states in this polymer.

The fluorescence quantum yields of the polymers were also determined in toluene solutions. These were determined on comparison with the solution emission of quinine sulfate dihydrate ($\Phi_{fl} = 0.546$) used as a standard. The quantum yields of fluorescence for these polymers are shown in Table 1. Polymer **P1** displayed a fluorescence quantum yield Φ of 0.53 while that of polymer **P2** showed a significantly lower fluorescence quantum yield Φ of 0.14. Measurements of the fluorescence quantum yields were also undertaken in the solid state using an integrating sphere and were found to be 0.05 ± 0.005 for polymer **P1** and 0.07 ± 0.004 for polymer **P2**. Clearly, the solid-state quantum efficiencies that we deduce are significantly lower than those determined in solution. The lower fluorescence efficiency observed in solid films results from the fact that, in the solid state, excitons are able to undergo energy migration between polymer molecules,[17] and as such have a much higher probability for quenching at nonradiative defect sites.[15] Such defect states in solid films may result from the intrinsic properties of the molecular film (such as excimer or aggregate states) or may originate from extrinsic effects such as residual oxidation. The effect of nonradiative defect sites on radiative recombination is significantly reduced in solution, as the formation of excimer or aggregate states is suppressed. Furthermore, diffusion to extrinsic quenching sites is also suppressed in solution as excitations are largely confined to a single molecule and are unable to undergo intermolecular diffusion.

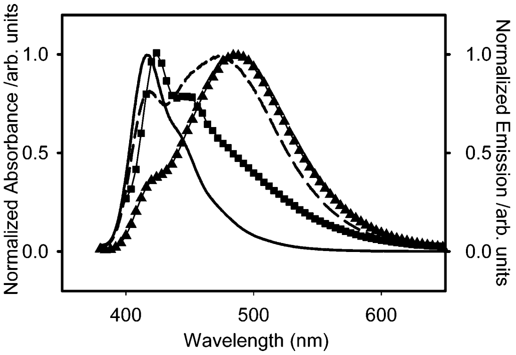


Figure 3. PL spectra of **P1** in toluene (solid line), THF (dashed line), dichloromethane (triangles), and film (squares).

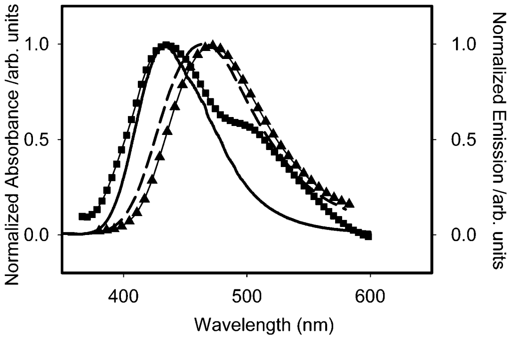


Figure 4. PL spectra of **P2** in toluene (solid line), THF (dashed line), dichloromethane (triangles), and film (squares).

Effects of Solvent Polarity on the Fluorescence of the Polymers. In addition to the fluorescence studies on polymers **P1** and **P2** in toluene, measurements were also conducted in dichloromethane and tetrahydrofuran. While the electronic spectra of polymers **P1** and **P2** are identical, irrespective of whether they were run in toluene, dichloromethane, or THF, the fluorescence measurements of these materials reveal major differences in their spectral features in different solvents (Table 2). While there is one main emission band at 417 nm with a shoulder at 441 nm for polymer **P1** in toluene, the fluorescence spectrum of **P1** in THF displays an emission band at 418 nm together with a more prominent broad emission band at 473 nm. The fluorescence spectrum of **P1** in dichloromethane displays a weak emission band at 417 nm and a very prominent broad emission band at 486 nm (Figure 3). It is worth noting that the red-shifted emission bands for **P1** in solution in THF and in dichloromethane are not present in the spectra of the polymer as a film and it is also important to note that they are not concentration-dependent. It is evident from these results that the solvent polarity plays a major role in the fluorescence properties of these materials and it could be postulated that the emission band at around 417 nm originates from a different excited state from those at 473 or 486 nm and that their intensities are dependent on the polarity of the solvent. The fluorescence properties of polymer **P2** are also subject to the same solvent effects. Its emission maxima are also red-shifted when in solution in THF and dichloromethane compared to when it is in solution in toluene (Figure 4). Given that that the red-shifted emission bands remain unchanged even at very low concentrations and given that these bands are not observed in films, it is reasonable to exclude that they are due to aggregation and excimer emission. In the literature,[18] there are a number of examples of molecules which present similar behavior and which show changes in their fluorescence depending on the solvent polarity. Twisted intramolecular charge-transfer states and structures were proposed as a possible explanation for these observations. Studies on *N*-(1-naphthyl)-carbazole and *N*-(2-

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(18) Grabowski, Z. R.; Rotkiewicz, K.; Rettig, W. *Chem. Rev.* **2003**, *103*, 3899.

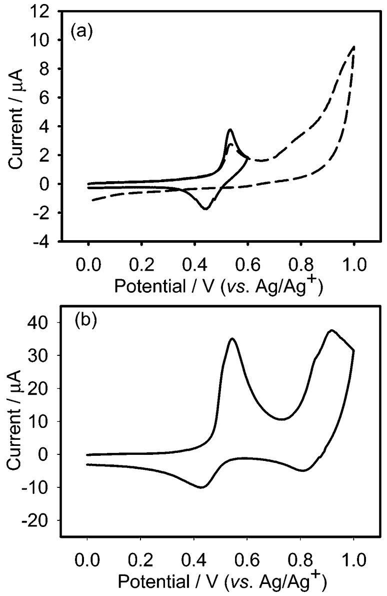

Figure 5. Cyclic voltammetry curves of thin films of (a) **P1** cycling up 0.6 V (solid line) and cycling up to 1.0 V (dashed line) and (b) **P2** on platinum disc electrodes (area 0.031 cm^2) at a scan rate of 100 mV s^{-1} in acetonitrile/tetrabutyl ammonium perchlorate (0.1 mol dm^{-3}).

Table 3. Redox Potentials of P1 and P2 in 0.1 M TBAClO$_4$/CH$_3$CN on Pt Working Electrode at 100 mV s^{-1} Using Ag/Ag$^+$ Reference Electrode

polymer	E_{pa}/V	E_{pc}/V	$I_P{}^a$/eV
P1	0.54 0.81^b	0.44	5.0
P2	0.54, 0.86,^{c} 0.92	0.43, 0.81	5.1

^{a} Ionization potential (vs vacuum) determined from onset of oxidation. ^{b} Irreversible oxidation wave. ^{c} Shoulder oxidation peak.

naphthyl)-carbazole[19] have shown that the emission wavelengths of these materials were very sensitive to the solvents polarity and intramolecular charge transfer. Similarly, 4-aminodiphenyl amines[20] showed similar behavior. The extra red-shifted emission bands which are observed for polymers **P1** and **P2** could perhaps be due to intramolecular charge-transfer states associating the strongly electron-donating 4-dialkylamino phenyl substituents and the carbazole repeat units on the polymer chains; however, we are not in a position to confirm this hypothesis with the available data.

Electrochemical Studies. Investigations of the electrochemical properties of polymers **P1** and **P2** were also undertaken. Cyclic voltammetry measurements on drop-cast polymer films were conducted in acetonitrile with tetrabutylammonium perchlorate as an electrolyte. The cyclic voltammograms of polymers **P1** and **P2** are shown in Figure 5. The redox potentials of the various polymers as well as their respective ionization potentials (vs vacuum) are shown in Table 3.

The redox behavior of polymer **P1** indicates a reversible redox wave with an oxidation wave at the potential $E_{pa} = 0.54$ V and an associated reduction wave at a potential E_{pc} at 0.44 V (Figure 5a solid line). The oxidative reversibility of polymer **P1** is maintained on repeated cycling between 0.0 and 0.7 V (vs Ag/Ag$^+$). However, this reversibility is lost if cycling goes beyond 0.7 V with an irreversible oxidation wave appearing at 0.81 V (vs Ag/Ag$^+$) (Figure 5a, dashed line). This behavior indicates that there are two separate oxidation processes: the first one being attributed to the reversible oxidation of the 4-dialkylamino phenyl substituent and the second one to that of the carbazole polymer backbone which is irreversible as the 3,6-positions on carbazole repeat units in polymer **P1** are still sensitive to side reactions at high potentials. This was the case for poly(9-alkyl-9*H*-carbazole-2,7-diyl)s described in earlier studies which under similar conditions only showed the irreversible oxidation waves and a loss of electroactivity attributed to the formation of new species as a result of the creation of new linkages between the 3,6-positions of adjacent polymer chains within the films.[21] It is also worth noting that cyclic voltammetry studies in acetonitrile solutions of monomers **1a** and **4a** have shown that while monomer **4a** showed a reversible redox wave with an oxidation wave at $E_{pa} = 0.50$ V and an associated reduction wave at $E_{pc} = 0.41$ V, monomer **1a**, which does not have a 4-dialkylamino-phenyl group, showed no redox waves between 0 and 0.7 V. This indicates that the first oxidation wave in the cyclic voltammetry curves of polymer **P1** (at $E_{pa} = 0.54$ V and $E_{pc} = 0.44$) are indeed attributed to its 4-dialkylamino-phenyl groups.

The cyclic voltammogram of polymer **P2** indicates an oxidation wave at 0.54 V and an associated reduction wave at 0.43 V (vs Ag/Ag$^+$); in addition, oxidation waves at 0.86 and 0.92 V with an associated reduction wave at 0.81 V (vs Ag/Ag$^+$) can also be seen on the CV traces. We attribute the first oxidation wave to the reversible oxidation of the 4-dialkylamino phenyl substituents and the second one to that of the carbazole polymer backbone which is reversible in the case of polymer **P2** as the 3,6-positions on alternate carbazole repeat units are protected with methyl substituents which should reduce side reactions involving the formation of new species occurring as a result of the creation of new linkages between the 3,6-positions of adjacent polymer chains within the films from carbazole repeat units with no methyl substituents on the copolymer chains.

The ionization potential (vs vacuum) of polymer **P1** was estimated from the onset of its oxidation in cyclic voltammetry experiments as 5.0 eV (on the basis that ferrocene/ferrrocenium is 4.8 eV below the vacuum level[22]). The ionization potential (vs vacuum) of polymer **P2** was estimated on the same basis as 5.1 eV. This ionization potential is similar to that of **P1** as both polymers have 4-dialkylamino phenyl substituents which oxidize before the polymer backbones at similar potentials. The ionization potentials of polymers **P1** and **P2** are lower than those of poly(9-alkyl-9*H*-carbazole-2,7-diyl)s[9] described in earlier studies (5.0 and 5.1 eV vs 5.4 eV). They are also respectively 0.8 and 0.7

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eV lower than those of poly(9,9-dioctyl-fluorene-2,7-diyl).[6] This could suggest an easier hole injection into films from ITO electrodes in electronic device applications.

Conclusion

The preparation and characterization of new classes of 2,7-linked carbazole main chain conjugated polymers with 4-dialkylamino-phenyl substituents has been realized. Poly(9-(4-dioctylamino-phenyl)-9*H*-carbazole-2,7-diyl), **P1**, and poly(3,6-dimethyl-9-(4-dioctylamino-phenyl)-9*H*-carbazole-alt-9-(4-dioctylamino-phenyl)-9*H*-carbazole-2,7-diyl), **P2**, were prepared through Suzuki coupling methodologies. Polymer **P1** was obtained with high average molecular weight values with a degree of polymerization of ∼190 for fractionated samples which represents one of the highest values described for these classes of 2,7-linked carbazole main chain conjugated polymers. Polymer **P2** had a lower degree of polymerization as a result of the steric effects of the methyl substituents at the 3,6-positions on monomer **4b**, which impeded the polymerization reaction. Polymers **P1** and **P2** emit in the blue part of the electromagnetic spectrum in solution in toluene. Films of **P1** also emit in the blue part of the electromagnetic spectrum while those of **P2** emit in the blue/green. The fluorescence of both polymers is solvent-dependent and is red-shifted in polar solvents like dichloromethane and tetrahydrofuran unlike other classes of poly(9-alkyl-9H-carbazole-2,7-diyl) polymers which do not show fluorescence solvent dependency. Polymer **P1** showed a good oxidative reversibility up to 0.7 V (vs Ag/Ag$^+$); however, an irreversible oxidation wave appeared at 0.81 V, indicating the sensitivity of the 3,6-positions on carbazole repeat units in polymer **P1** to side reactions at high potentials. Polymer **P2** showed good oxidative reversibility up to 1.0 V (vs Ag/Ag$^+$) with distinct oxidation waves for respectively the 4-dialkylamino phenyl substituents and the backbone of the polymer, which indicate the stabilizing effect of methyl substitution on this class of carbazole materials. The ionization potentials of polymers **P1** and **P2** are respectively 5.0 and 5.1 eV, which are very favorable values for hole injection when such materials are used in electronic devices. Further studies are underway to elucidate the origin of the red shifts observed in polar solvents and also on the optimization of analogous materials with higher fluorescence quantum yields.

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