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Synthesis and Characterization of Blue Light Emissive Carbazole Containing Perfluorocyclobutyl Aryl Ether Polymers

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ABSTRACT: A series of N-alkyl/aryl carbazole 3,6-substituted aryl trifluorovinyl ether (TFVE) monomers were synthesized in high purity and yield from a concise four-step synthesis using carbazole as a starting material. Condensate-free, step-growth chain extension of the monomers afforded perfluorocyclobutyl (PFCB) aryl ether homo- and copolymers as solution processable, optically transparent blue light emissive materials. Aryl TFVE monomers and conversion to PFCB aryl ether polymers were structurally elucidated and purified by HRMS, NMR (1H, 13C, and 19F), GPC, and ATR-FTIR. Thermal analysis by DSC and TGA revealed glass transition temperatures > 150 °C and onset of decomposition in nitrogen > 410 °C with 40 wt % char yield up to 900 °C. Optical studies included solution (in THF) and solid state (spin cast thin film) UV-Vis and fluorescence spectroscopy and showed structure dependence of these blue emissive systems by the nature of the N-alkyl/aryl carbazole substitution in either homo- or copolymers configurations.

INTRODUCTION

Superior hole-transporting mobility and excellent photoconductivity properties of carbazole-containing polymers place them among the one of the most studied materials for optoelectronic applications.1-3 They have been commercialized in a number of devices and process applications such as photocopiers, laser printers, and holographic security stamps.4 This is due to the electron-donating capabilities associated with the nitrogen in the carbazole. The carbazole moiety can easily form relatively stable radical cations (holes) exhibiting relatively high charge carrier mobilities. The carbazole ring can easily be substituted to obtain high thermal and photochemical stability. These are particularly attractive materials since they are cheap raw materials readily obtained from commercial feedstock, such as coal-tar distillation. Recently, there is increased interest in the carbazole moiety being introduced as a convenient building block for the design and synthesis of new structures of carbazole-containing conjugated polymers.5-7 Architectures include carbazoles either as a pendant group or as a main chain member. The versatility to produce such homopolymers as well as copolymers provides access to novel electro luminescent materials for polymer light-emitting diodes (PLEDs) and new host materials for the high efficiency phosphorescent (triplet emitter) in PLEDs.

Organic polymers, in particular fluoropolymers, are emerging as viable alternatives to traditional inorganic materials in components for optical communication technologies.8 Polymeric materials offer improved integratability with other materials, flexibility in processing, and lower fabrication cost. Among the various polymeric optical materials, perfluorocyclobutyl (PFCB) aryl ether polymers are an emerging, versatile class of partially fluorinated linear and network polymers derived from the condensate-free cyclodimerization of aryl trifluorovinyl ether (TFVE) monomers (see general Scheme 1).9 PFCB aryl ether polymers retain many
classical properties of fluoropolymers, including low optical attenuation and high thermal performance, while offering many advantages such as highly tailorable refractive index for the core and cladding and excellent solution processability. Other partially fluorinated polyaryl ethers produced by chain extension of bisphenols with perfluorocycloolefins[1] and aryl TFVEs[2] have also demonstrated excellent solution processability and tailoring ability of the backbone for a multitude of applications. Specific to the scope of this work, semifluorinated polyaryl ethers of this nature have served as a suitable host materials for photonic applications whereby isolated chromophore covalently anchored in their backbone demonstrate uncompromised optical responses from light or electrical excitation. [3] [5]

The preparation of the majority of functionalized poly(carbazolyl) employs costly metal-mediated coupling and consequently by the rigid nature of the chain extended systems often produces difficult to solution process oligomeric/polymeric systems.[6] [8] While fluoropolymers possess superior performance benefits over their hydrogen containing analogs, they have shown little utility for light emissive applications because of their inherent poor solution processability and their lack of extended aromatic conjugation. However, it has been demonstrated that introducing partial fluorine into conjugated polymer systems improves their resistance to photocrosslinking.[9] For these reasons, there remains a need for easily prepared, solution processable fluoropolymers capable of efficient light emission. Indeed, several linear and crosslinked aryl amine derived PFCB aryl ether polymer systems have been specifically prepared for hole-transport materials.[20] [22] This work presents the first concise monomer-polymer synthesis and thermal and optical properties of a functionalized partially conjugated PFCB aryl ether polymer with N-alkyl/aryl substituted carbazoles as isolated chromophores into the main chain.

EXPERIMENTAL SECTION

Instrumentation. 1H, 13C, and 19F NMR spectra were recorded on a JEOL Eclipse 300 (300 MHz for 1H, 75 MHz for 13C, and 283 MHz for 19F) in CDCl3. Chemical shifts were reported in δ ppm with reference to internal tetramethylsilane (0 ppm), CDCl3 (77 ppm), and CFCl3 (0 ppm) for 1H, 13C and 19F nuclei, respectively. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) analysis of neat samples was performed on a Thermo-Nicolet Magna 550 FTIR spectrophotometer with ATR attachment. High resolution mass spectra (HRMS, FAB+) were obtained at the University of Illinois Mass Spectrometry Laboratory (Urbana-Champaign, IL) on a 70-SE-4F Mass spectrometer. Differential scanning calorimetry (DSC) analysis and thermal gravimetric analysis (TGA) were performed on a TA Q1000 instrument and Mettler-Toledo 851 instrument, respectively, both at a heating rate of 10 °C/min in nitrogen. The glass transition temperature (Tg) was obtained from a second heating cycle, the reported Tg values were taken at the midpoint of the C0 curve. Gel permeation chromatography (GPC) data were collected in CHCl3 using polystyrene as a standard (Polymer Labs Basical PS-2) using a Waters 2690 Alliance System with UV-Vis detection at 35 °C. Absorbance and emission were collected using a Varian Cary 50 Bio UV-vis spectrophotometer and a Varian Cary Eclipse spectrophotofluorometer. Thin film absorption and emission data were collected on a Perkin-Elmer Lambda 950 spectrophotometer and Jobin-Yvon Fluorolog Tau-3 spectrophotofluorometer, respectively. Slit widths were kept constant for emission measurements.

General Methods and Materials. All reactions were carried out under nitrogen (passed over CaSO4) and used for all synthetic manipulations. Chemicals and solvents used were purchased from Sigma Aldrich or Alfa Aesar and used without purification unless otherwise stated. 4-Bromo(trifluorovinyl)benzene 6 was donated and also commercially available from
Tetramer Technologies, LLC (Pendleton, SC) and distributed by Oakwood Chemicals, Inc. (Columbia, SC). 4,4'-5,5'-Tetramethyl-2-(4-trifluoromethoxy-phenyl)-1,3,2-dioxaborolene 4 was synthesized according to a procedure reported elsewhere\(^4\) and is commercially available from Oakwood Chemicals, Inc. (Columbia, SC). HPLC grade tetrahydrofuran (THF) and diethyl ether (Et\(_2\)O) were dried and deoxygenated using a Pure-Solv solvent purification system from Innovative Technologies. Silica gel column chromatography was performed using Sorbent Silicagel (220-450 mesh, Sorbent Technology). Thin layer chromatography (TLC) was carried out on polyester support plates coated with silica gel 60F254 (Aldrich).

9-Octylcarbazole (2a). To a stirred solution of carbazole 1 (20 g, 0.12 mol) and phase-transfer catalyst benzyltriethylammonium chloride (0.8 g, 3.51 mmol) in toluene (100 ml) was added portion wise 10 wt % aqueous NaOH (70 g, 1.75 mol). n-Octylbromide (27.7 g, 0.14 mol) was added drop wise and the reaction mixture was then heated to reflux for 16 hrs. The organic layer was separated, washed with water, dried over anhydrous MgSO\(_4\), vacuum filtered, and concentrated by rotary evaporation. Excess n-octylbromide was removed by vacuum distillation and the title compound was obtained after column chromatography (SiO\(_2\), hexane/ethylamine, 98/2 (v/v), R\(_f\) = 0.45) as a colorless viscous oil (29.6 g, 88%). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 8.27 (d, \(J = 7.5\) Hz, 2H), 7.61 (t, \(J = 7.5\) Hz, 2H), 7.53 (d, \(J = 8.2\) Hz, 2H), 7.39 (t, \(J = 7.5\) Hz, 2H), 4.35 (t, \(J = 7.2\) Hz, 2H, N-CH\(_2\)), 2.01-1.96 (m, 2H), 1.48-1.42 (m, 10H), 1.05 (t, \(J = 6.9\) Hz, 3H, -CH\(_3\)). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 140.7, 125.8, 123.1, 120.6, 119.0, 108.9, 43.3, 32.1, 29.7, 29.5, 29.3, 27.6, 23.0, 14.4.

9-(4-Tolyl)-carbazole (2b). Carbazole 1 (10.0 g, 56.8 mmol), 4-isodotoluene (10.44 g, 47.3 mmol), KOH flakes (21.1 g, 0.378 mol), CuCl (0.5 g, 5.05 m), and 1,10-phenanthroline (0.5 g, 2.78 mmol) in toluene (50 ml) were refluxed for 24 h. The reaction mixture was poured into water and extracted with DCM. The combined organic layers were washed sequentially with 1M HCl, 1M NH\(_4\)OH, and water, dried over anhydrous MgSO\(_4\), and concentrated by rotary evaporation. The title compound was purified by column chromatography (SiO\(_2\), hexane/dichloromethane, 4:1 (v/v), R\(_f\) = 0.40) and recrystallized from hexane/DCM to afford white needle-like crystals (9.4 g, 76%). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 8.14 (d, \(J = 7.9\) Hz, 2H), 7.43-7.39 (m, 8H), 7.29 (d, 2H, \(J = 8.2\) Hz), 2.49 (s, 3H, -CH\(_3\)). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 141.1, 137.4, 135.2, 120.6, 127.1, 125.9, 123.3, 120.4, 119.8, 109.9, 21.4.

9-(4-Methoxy)phenyl-carbazole (2c). The title compound was synthesized following the procedure for the preparation of 2b using 4-iodoanisole affording white needle-like crystals (65%). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 8.13 (d, 2H, \(J = 7.7\) Hz), 7.46-7.27 (m, 8H), 7.09 (d, 2H, \(J = 9.7\) Hz), 3.91 (s, 3H, -OCH\(_3\)). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 158.9, 141.5, 130.4, 128.7, 125.9, 123.2, 120.4, 119.7, 115.2, 109.8, 55.7.

3,6-Dibromo-9-octylcarbazole (3a). N-Bromosuccinimide (1.24 g, 69.8 mmol) was slowly added to 9-octylcarbazole 2a (10.0 g, 35.8 mmol) in THF (200 ml) at 0 °C. The mixture was allowed to warm to room temperature and allowed to stir for 16 h. The THF was removed by rotary evaporation and the solid residue was dissolved in diethyl ether and washed with water. The organic layer was dried (MgSO\(_4\)), vacuum filtered, and concentrated by rotary evaporation. Purification by column chromatography (SiO\(_2\), hexane/dichloromethane, 99:1 (v/v), R\(_f\) = 0.5) afforded the title compound as white crystals (12.0 g, 76%). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 8.10 (s, 2H), 7.55 (ddd, \(J = 2.7\) Hz, 8.6 Hz, 2H), 7.23 (d, \(J = 8.6\) Hz, 2H), 4.38 (t, \(J = 6.9\) Hz, 2H, -NCH\(_2\)), 1.83-1.68 (m, 2H), 1.29-1.22 (m, 10H), 0.83 (t, \(J = 6.9\) Hz, 3H, -CH\(_3\)). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta\) 139.4, 129.1, 123.5, 123.3, 112, 110.5, 43.4, 31.8, 29.4, 29.2, 28.9, 27.3, 22.7, 14.2.

3,6-Dibromo-9-[4-tolyl]-carbazole (3b). The title compound was synthesized by adapting a previously reported procedure\(^{25}\) following the preparation of 3a affording white needle-like
crystals (9.4 g, 53%) by recrystallization from hexane/DCM mixture solvent. **H NMR (CDCl3, 300 MHz)**: δ 8.18 (s, 2H), 7.47 (d, 2H), 7.39 (d, 2H), 7.36 (d, 2H), 7.20 (d, 2H), 2.49 (s, 3H, -CH3); **13C NMR (75 MHz, CDCl3)**: δ 138.2, 134.2, 130.8, 129.4, 126.9, 123.9, 113.0, 111.6, 21.4.

**3,6-Dibromo-9-[4-methoxy]phenyl]carbazole (3c).** The title compound was synthesized following the procedure for the preparation of 3a affording a white solid (88%). **H NMR (CDCl3, 300 MHz)**: δ 8.15 (s, 2H), 7.47 (d, 2H, J = 8.9 Hz), 7.35 (d, 2H, J = 8.6 Hz), 7.15 (d, 2H, J = 8.6 Hz), 7.08 (d, 2H, J = 8.6 Hz), 3.91 (s, 3H, -OCH3); **13C NMR (75 MHz, CDCl3)**: δ 159.4, 140.4, 129.4, 128.5, 123.8, 123.2, 115.4, 112.9, 115.5, 55.7.

**Bis[9-octylcarbazole-3-yl](2d).** Anhydrous iron(III) chloride (23.2 g, 144 mmol) was added portion-wise to a stirred solution of 2a (20.0 g, 71.9 mmol) in chloroform (400 mL). After 24 h, water was added and the organic layer was separated, washed with water, dried over MgSO4, filtered, and concentrated using rotary evaporation. The mixture was purified by column chromatography (SiO2, hexane/dichloromethane/triethylamine, 75/25/1, v/v/v), Rf = 0.35 and crystallization from hexane/dichloromethane to afford the title compound as white crystals (2.59 g, 61%). **H NMR (CDCl3, 300 MHz)**: δ 8.40 (d, J = 1.7 Hz, 2H), 8.16 (d, J = 7.6 Hz, 2H), 7.79 (dd, J = 1.7 Hz, 8.2 Hz, 2H), 7.47–7.41 (m, 6H), 7.23 (dt, J = 1.7 Hz, 7.6 Hz, 2H), 4.26 (t, J = 7.2 Hz, 4H), 1.90–1.85 (m, 4H), 1.36–1.24 (m, 20H), 0.84 (t, J = 6.9 Hz, 6H); **13C NMR (CDCl3, 75 MHz)**: δ 141.0, 139.7, 133.5, 125.8, 125.7, 123.5, 120.6, 119.1, 118.9, 109.1, 108.9, 43.3, 32.0, 29.6, 29.4, 29.2, 27.5, 22.8, 14.3.

**Bis[9-(4-methoxyphenyl]carbazol-3-yl](2e).** The title compound was synthesized following the procedure for the preparation of 2d using 2b and purification by column chromatography (SiO2, hexane/dichloromethane/triethylamine, 60/39/1, v/v/v), Rf = 0.35 and crystallization (hexane/dichloromethane) afforded white crystals (4.10 g, 50%). **H NMR (CDCl3, 300 MHz)**: δ 8.13 (d, 2H, J = 7.7 Hz), 7.46–7.27 (m, 8H), 7.14 (d, 2H, J = 9.7 Hz), 3.89 (s, 6H, -OCH3); **13C NMR (75 MHz, CDCl3)**: δ 159.0, 141.9, 140.6, 134.3, 130.5, 128.6, 126.1, 125.9, 123.9, 123.5, 120.5, 119.9, 119.0, 115.2, 110.1, 109.9, 55.7.

**Bis[6-bromo-9-octylcarbazol-3-yl](3d).** The title compound was synthesized by following the preparation of 3a using 2d and purification by column chromatography (SiO2, hexane/dichloromethane, 90/10, v/v), Rf = 0.35 and crystallization (hexane/dichloromethane) afforded a pale yellow solid (64%). **H NMR (CDCl3, 300 MHz)**: δ 8.33 (d, 2H, J = 1.4 Hz), 8.30 (d, 2H, J = 2.1 Hz), 7.82 (dd, 2H, J = 1.7, 8.6 Hz), 7.55 (d, 2H, J = 2.0 Hz), 7.45 (d, 2H, J = 8.6 Hz), 7.26 (d, 2H, J = 8.6 Hz), 4.23 (t, J = 7.2 Hz, 4H), 1.90–1.85 (m, 4H), 1.36–1.24 (m, 20H), 0.88 (t, J = 6.9 Hz, 6H); **13C NMR (CDCl3, 75 MHz)**: δ 159.2, 140.6, 134.3, 129.9, 128.8, 128.5, 126.5, 125.1, 123.2, 122.8, 119.9, 119.0, 115.3, 112.6, 111.4, 110.3, 43.4, 31.9, 29.6, 29.3, 29.1, 27.4, 22.8, 14.3.

**Bis[6-bromo-9-(4-methoxyphenyl]carbazol-3-yl](3e).** The title compound was synthesized by following the preparation of 3a using 2e and purification by column chromatography (SiO2, hexane/dichloromethane, 44/56, v/v), Rf = 0.4 and crystallization (hexane/dichloromethane) afforded a white solid (74%). **H NMR (CDCl3, 300 MHz)**: δ 8.37 (d, 2H, J = 1.4 Hz), 8.33 (d, 2H, J = 2.1 Hz), 7.73 (dd, 2H, J = 1.7, 8.6 Hz), 7.47 (dd, 2H, J = 1.7, 8.6 Hz), 7.44 (d, J = 2.1 Hz, 2H), 7.43 (d, J = 2.1 Hz, 2H), 7.20 (d, J = 8.6 Hz, 2H), 7.11 (d, J = 8.9 Hz, 4H), 3.93 (s, -OCH3, 6H); **13C NMR (75 MHz, CDCl3)**: δ 159.2, 140.6, 134.3, 129.9, 128.8, 128.5, 126.5, 125.1, 123.2, 122.8, 119.5, 119.0, 115.3, 112.6, 111.4, 110.3, 55.7.

**General Synthetic Procedure of Carbazole Aryl Trifluorovinyl Ether Monomers (5a–5e) via the Pol(0) Catalyzed Suzuki Coupling of 3a–3e with 4.** Compounds 3a–3e (5.0 mmol), 4 (1.18 g, 10.6 mmol), and 2 M K2CO3 (17 mL) in THF (35 mL) was degassed with nitrogen. Pol(PPh3) (0.231 g, 0.2 mmol) was subsequently added to the mixture and refluxed for 24 h in the absence of light. The reaction mixture was then extracted with diethyl ether, the organic layer
washed with 1 M HCl solution, dried over anhydrous MgSO₄ and concentrated by rotary evaporation. The reaction mixture was further purified by chromatography (SiO₂, hexane/dichloromethane, 4/1 [v/v]) and recrystallized from hexane/dichloromethane to afford 5a–5e.

3.6-Bis(4-(1,2,2-trifluorovinyl)oxy)phenyl]-9-octyl-9H-carbazole (5a). White powder (2.3 g, 73%); Mp 63 °C (DSC); ATR-FTIR (neat): v 3043, 2930, 2854, 1830 (w, CF=CF₂), 1604, 1510, 1311 (s, br), 1165 (s, br), 833, 807 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 8.28 (d, J = 1.7 Hz, 2H), 7.69 (dd, J = 1.7 Hz, 8.2 Hz, 2H), 7.63 (dd, J = 1.7 Hz, 8.2 Hz, 2H), 7.42 (d, J = 8.3 Hz, 4H), 7.19 (d, J = 8.3 Hz, 4H), 4.26 (t, 2H, CH₂CO₂H), 1.90–1.80 (m, 2H); 13C NMR (75 MHz, CDCl₃): δ 154.3, 140.5, 139.1, 131.4, 128.8, 125.4, 123.5, 118.9, 116.4, 109.3, 43.4, 31.0, 29.5, 29.2, 27.4, 22.7, 14.2; ¹³C NMR (283 MHz, CDCl₃): δ 8.197 (dd, cis-CF=CF₂, 2F, F₂), -126.5 (dd, trans-CF=CF₂, 2F, F₂), -133.4 (dd, CF=CF₂, 2F, F₂) (J₉ = 95.4 Hz, J₈ = 55.9 Hz, J₇ = 108.5 Hz); HRMS (FAB⁺) Calculated (Found) for C₃₈H₂₄O₃F₆ 623.2262 (623.2260).

3.6-Bis(4-(1,2,2-trifluorovinyl)oxy)phenyl]-9-p-tolyl-9H-carbazole (5b). White solid (1.7 g, 57%); Mp 94, 128 °C (DSC); ATR-FTIR (neat): v 3040, 2924, 2852, 1381 (w, CF=CF₂), 1604, 1510, 1311 (s, br), 1168 (s, br), 835, 799 cm⁻¹; ¹H NMR (300 MHz, CDCl₃): δ 8.33 (d, J = 1.7 Hz, 2H), 7.69 (dd, J = 2 Hz, 8.3 Hz, 4H), 7.62 (dd, J = 1.7 Hz, 8.3 Hz, 2H), 7.42–7.49 (m, 6H), 7.20 (d, J = 8.3 Hz, 4H), 2.51 (s, 3H, CH₃); ¹¹C NMR (75 MHz, CDCl₃): δ 154.2, 141.1, 139.0, 137.8, 134.9, 132.4, 130.7, 128.8, 125.9, 123.9, 113.8, 116.4, 120.4, 21.4; ¹³C NMR (283 MHz, CDCl₃): δ 8.197 (dd, cis-CF=CF₂, 2F, F₂), -126.5 (dd, trans-CF=CF₂, 2F, F₂), -133.4 (dd, CF=CF₂, 2F, F₂) (J₉ = 95.4 Hz, J₈ = 55.9 Hz, J₇ = 108.5 Hz); HRMS (FAB⁺) Calculated (Found) for C₃₈H₂₄O₃F₆ 623.2262 (623.2260).
(a, 2H), 8.39 (s, 2H), 7.87 (d, J = 8.3 Hz, 2H), 7.78 (dd, J = 1.7 Hz, 8.6 Hz, 2H), 7.71 (d, J = 8.6 Hz, 4H), 7.50 (d, J = 1.7 Hz, J = 8.6 Hz, 2H), 7.31 (d, J = 8.6 Hz, 4H), 7.40 (dd, J = 1.7 Hz, 8.6 Hz, 4H). 13C NMR (75 MHz, CDCl3): δ 159.1, 141.4, 141.1, 139.1, 134.3, 132.2, 130.3, 128.8, 128.5, 126.1, 125.4, 124.0, 123.9, 119.0. 118.9, 116.4, 115.3, 110.3, 55.7. 19F NMR (283 MHz, CDCl3): δ -119.7 (dd, cis- CF=CF2, Fδ, Fα), -126.5 (dd, trans- CF=CF2, Fδ, Fα), -133.4 (dd, CF=CF2, Fδ, Fα) (Jαα = 95.4 Hz, Jαβ = 55.9 Hz, Jβα = 108.5 Hz). HRMS (FAB) Calculated (Found) for C24H14O2N2F2: 888.24226 (888.24250).

General Polymerization for the Preparation of Homopolymers P5a-P5e and Copolymers with 6 (Scheme 3). Weighed, vacuum-dried monomers 5a–5e (and 6) were added to a flame-dried glass ampule that was allowed to cool in a desiccator. The ampule was placed under high vacuum using a manifold, flame-sealed, and then placed in a pre-heated sand bath at 180 °C for 48 hours. After cooling to room temperature, the ampule was then opened and the transparent, solid material was dissolved into a minimum amount of THF. The dissolved solid product was precipitated in excess, cold methanol and washed several times with methanol, vacuum filtered, and dried in vacuum at 40 °C for 16 h affording white solid fibers in >95% yield.

P5a. ATR-FTIR (neat): ν 3050, 2925, 2850, 1603, 1510, 1170, 956 (cyclobutyl-F3), 828, 801 cm⁻¹. 1H NMR (300 MHz, CDCl3): δ 8.18 (s, 2H), 7.60-7.63 (m, 6H, aromatic H), 7.21-7.39 (m, 6H, aromatic H), 4.17 (t, 2H, -NCH3), 1.85-1.75 (m, 2H), 1.34-1.21 (m, 10H), 0.81 (t, 3H, -CH3). 19F NMR (283 MHz, CDCl3): δ trfluorovinyl endgroups at -118.9 (2F, dd, cis- CF=CF2, Fδ, Fα), -126.5 (2F, dd, trans- CF=CF2, Fδ, Fα), -133.4 (2F, dd, CF=CF2, Fδ, Fβ, Fγ) (Jαα = 95.4 Hz, Jαβ = 59.2 Hz, Jβα = 108.5 Hz).

P5b. ATR-FTIR (neat): ν 3035, 2920, 2804, 1510, 1170, 956 (cyclobutyl-F3), 828, 802 cm⁻¹. 1H NMR (300 MHz, CDCl3): δ 8.26 (s, 2H), 7.60-7.63 (m, 6H, aromatic H), 7.22-7.39 (m, 10H, aromatic H), 2.46 (s, 3H, -CH3). 19F NMR (282.8 MHz, CDCl3): δ trfluorovinyl endgroups at -119.5 (2F, dd, cis- CF=CF2, Fδ, Fα), -126.5 (2F, dd, trans- CF=CF2, Fδ, Fα), -133.4 (2F, dd, CF=CF2, Fδ, Fα) (Jαα = 95.4 Hz, Jαβ = 59.2 Hz, Jβα = 108.5 Hz), broad at 128.0-132.9 (m, cyclobutyl-F3).

P5c. ATR-FTIR (neat): ν 3037, 2920, 2804, 1604, 1510, 1170, 956 (cyclobutyl-F3), 835, 796 cm⁻¹. 1H NMR (300 MHz, CDCl3): δ 8.36 (d, 2H, J = 7.9 Hz), 8.27 (d, 2H, J = 8.3 Hz), 7.23-7.80 (m, 16H, aromatic H), 4.23 (t, 4H, -NCH3), 1.85-1.75 (m, 4H), 1.40-1.21 (m, 20H), 0.84 (t, 6H, -CH3). 19F NMR (282.8 MHz, CDCl3): δ trfluorovinyl endgroups at -119.5 (2F, dd, cis- CF=CF2, Fδ, Fα), -126.5 (2F, dd, trans- CF=CF2, Fδ, Fα), -133.3 (2F, dd, CF=CF2, Fδ, Fβ, Fγ) (Jαα = 95.4 Hz, Jαβ = 59.2 Hz, Jβα = 108.5 Hz), 127.9-132.8 (m, cyclobutyl-F3).

P5d. ATR-FTIR (neat): ν 3046, 2920, 2850, 1604, 1510, 1170, 956 (cyclobutyl-F3), 835, 796 cm⁻¹. 1H NMR (300 MHz, CDCl3): δ 8.36 (d, 2H, J = 7.9 Hz), 8.27 (d, 2H, J = 8.3 Hz), 7.23-7.80 (m, 16H, aromatic H), 4.23 (t, 4H, -NCH3), 1.85-1.75 (m, 4H), 1.40-1.21 (m, 20H), 0.84 (t, 6H, -CH3). 19F NMR (282.8 MHz, CDCl3): δ trfluorovinyl endgroups at -119.5 (2F, dd, cis- CF=CF2, Fδ, Fα), -126.5 (2F, dd, trans- CF=CF2, Fδ, Fα), -133.3 (2F, dd, CF=CF2, Fδ, Fβ, Fγ) (Jαα = 95.4 Hz, Jαβ = 59.2 Hz, Jβα = 108.5 Hz), 127.9-132.8 (m, cyclobutyl-F3).

P5e. ATR-FTIR (neat): ν 3037, 2920, 1604, 1510, 1170, 956 (cyclobutyl-F3), 835, 801 cm⁻¹. 1H NMR (300 MHz, CDCl3): δ 8.31-8.38 (m, 4H), 7.04-7.69 (m, 24H, aromatic H), 3.84 (s, 6H, -OCH3). 19F NMR (283 MHz, CDCl3): δ trfluorovinyl endgroups at -119.5 (2F, dd, cis- CF=CF2, Fδ, Fα), -126.5 (2F, dd, trans- CF=CF2, Fδ, Fα), -133.3 (2F, dd, CF=CF2, Fδ, Fβ, Fγ) (Jαα = 95.4 Hz, Jαβ = 59.2 Hz, Jβα = 108.5 Hz), 128.0-132.8 (m, cyclobutyl-F3).

P5a-co-6. ATR-FTIR (neat): ν 3040, 2920 (at), 2855, 1603, 1510, 1171, 970 (cyclobutyl-F3), 823, 803 cm⁻¹. 1H NMR (300 MHz, CDCl3): δ 8.22 (d, 4H, J = 7.4-7.6 Hz, aromatic H), 2.48 (s, 3H, -CH3). 19F NMR (283 MHz, CDCl3): δ trfluorovinyl endgroups at -118.9 (2F, dd, cis- CF=CF2, Fα), -126.5 (2F, dd, trans- CF=CF2, Fα), -134.1 (2F, dd, CF=CF2, Fδ, Fα) (Jαα = 95.4 Hz, Jαβ = 59.2 Hz, Jβα = 108.5 Hz), 127.7-132.9 (m, cyclobutyl-F3).
RESULTS & DISCUSSION

Any trifluorovinyl ether (TFVE) 3,5-carbazole derived monomers 5a-5e were prepared in overall good isolated yields (57-85%) employing a multi-step synthesis from carbazole 1 as shown in Scheme 1. Carbazole 1 underwent facile Alkylation/arylation with n-octylbromide, 4-iodotoluene, and 4-iodoanisole affording substituted carbazoles 2a-2c, respectively. Carbazole dyads 2d and 2e were prepared by oxidative ferric chloride-mediated coupling regiospecific at the 3-position. Bromine was installed on the 3,6-position of M-alkylated carbazoles 2a-2c and at the 6,6'-position of dyads 2d and 2e upon treatment of 2a-2e with Na-bromosuccinimide affording intermediates 3a-3e. The aryl TFVE monomer synthesis of 5a-5e was completed by Pd(0) Suzuki-coupling of 3a-3e and two equivalents of aryl TFVE boronic acid 4. Structure elucidation and purity of all intermediates and aryl TFVE monomers were confirmed by 1H, 13C, and 19F NMR, FTIR, and HRMS.

PFCB aryl ether homopolymers PSa-PSe were achieved by heating aryl TFVE monomers 5a-5e neat in vacuum sealed ampules at 180 °C for 48 hours (Scheme 3). Precipitation of the dissolved solid polymers in minimal amounts of THF in cold MeOH afforded white fibers in >85% isolated yield. The same procedure and yield were achieved for the preparation of random copolymers P[(5a-5e)-co-6]. Monomers 5a-5e were reacted with aryl TFVE monomer 6 in a ca. 30:70 mole feed ratio. Copolymers mole ratio were formulated in this way to achieve optimum, higher-number-average molecular weight (Mn) polymers based on GPC analysis. Homo- and copolymer molecular weights and their accompanying polydispersity indices (PDI) are summarized in Table 1. Polymerization by the conversion of the aryl TFVE AMX pattern to the PFCB was observed by 19F NMR (compare Figure S4 with Figure S7 or Figure S9). 1H NMR functional group peak area integration confirmed incorporation of carbazole units in the homopolymer main chain and the experimental feed ratio agreed with the calculated values (Table 1). Further evidence of PFCB polymerization was confirmed by solid state ATR-FTIR analysis with the fluoroalkene (-CF=CF2) vibrational stretch ca. 1380 cm⁻¹ of the carbazole monomer to the resulting PFCB ring breathing mode at 760 cm⁻¹ of the polymers (compare Figure S1 with Figure S2 or Figure S3). Homopolymers PSb-PSe produced oligomers with Mₙ
ranging 4600–5300 g/mol and the reactive aryl TFVE end-group moieties are observed in the $^{19}F$
NMR (Figure S7). Attempts failed to further chain advance homopolymers P5b–P5e by inducing
longer reaction times up to 6 days resulting in yellowing the of the crude solid material.
Copolymers of 5b-P5 with 6 provided the means of achieving higher molecular weights with
trace signatures of aryl TFVEs by $^{19}F$ NMR (Figure S9). Overall, homo- and copolymers produced
polymers with narrow PDI typical of step-growth polymerizations. However, the n-octyl
functionalized monomer 5a afforded complete conversion to the highest molecular weight
homopolymer P5a and copolymer P(5a-co-6) with a M, of 12500 and 14400 g/mol, respectively.
This result indicates the side chain alkyl moiety in 5a in comparison with the aryl substituted
monomers 5b–5e promotes backbone flexibility to promote full conversion resulting in the
highest molecular weights among the respective homo- and copolymer series. $^1$H NMR analysis
of homo- and copolymers confirmed the N-alkyl/aryl side chain groups remained intact and are
amenable to the thermal step-growth chain extension polymerization (compare Figure S6 with
Figure S8 or Figure S10).

Purified homopolymers P5a–P5e and copolymers P(5b–5e)-co-6 produced optically
transparent, solution processable films by spin or drop casting from THF or CHCl$_3$. Although
homopolymers P5b–P5e are low in molecular weight, they are still able to produce freestanding
spin-cast films. Because they possess aryl TFVE groups, their latent thermal reactivity
could lead to post-functionalization with other compatible PFCB-forming monomers. For all
carbazole monomers, DSC thermal analysis showed the initial melt transition leading to the
cyclodimerization event onset at ca. 150 °C with peak exotherms at ca. 210 °C (Figure S11).
The sharp melt transitions indicate high monomer purity which is further confirmed by calculated
graphical software analysis of > 95%. The third scan of purified homo- and copolymers
indicated they were entirely amorphous systems. Only n-octyl functionalized homopolymer
PSa and copolymer P(5a-co-6) produced a well-defined glass transition temperature ($T_g$) at
151 °C and 150 °C, respectively. As a reference, carbazole-free homopolymer 6 can be produced
with similar molecular weight range which produces a $T_g$ of 140 °C. Very broad $T_g$'s could be
observed for PSa, and P5e; however they could not be measured for the remaining homo- and
copolymer series (Table 1). These results indicate the N-alkyl/aryl side chains profoundly
influence the polymer morphology. It can be inferred the N-arylated PFCB aryl ether homo-
and copolymers possess better packing whereby the longer N-octyl side chains of PSa and P(5a-
co-6) induce higher void volume, albeit the M, of this series is slightly higher. Polymer
degradation studies were performed using thermogravimetric analysis (TGA) in nitrogen as
shown in Figure S12. Onset of degradation was not observed until > 410 °C for all carbazole
PFCB aryl ether homo- and copolymers, typical of the PFCB chain-extended polymers. There
appears to be no effect of side chain moieties, nor correlation when comparing homopolymer
PSa with P(5a-co-6) copolymer molecular weights. The thermal robustness of the carbazole-
based PFCB aryl ether systems in this study suggests compatibility with other N-alkyl/aryl side
chains and/or functionalized aryl TFVE for copolymers could be explored. Char yields varied
from 45% up to 75% at 1000 °C for the series of homo/copolymers and the onset of degradation;
reported char yields appeared independent of molecular weight effects and side chain
functionalization.

Absorption and emission spectroscopy were performed using dilute solutions in THF (ca.
10$^{-3}$ M) and solid films from spin coating of the PFCB aryl ether homo- and copolymers.
Selected measured optical properties are found in Table 1 for polymers PSa-P5e and
P(5a–5e)-co-6. Solution absorption spectra of all polymers display a discrete π→π* transition
at 290–310 nm indicative of the carbazole unit. Thin films demonstrated two distinct π→π*
transitions at 260–269 nm and 297–320 nm representative of the biphenyl and carbazole
moieties, respectively. Modest red-shifting at ca. 8 nm was observed between the solution and thin films with the homo- and copolymers series. Optical band gaps (ΔE) are reported in Table 2 by the onset of excitation and were on average 4.4 eV in solution and consequently lowered to 3.5 eV in the solid state. These values are consistent with reported poly(carbazole)s and isolated carbazoles in poly(arylene ether)s.24 Onset excitation in solution was consistently lower for dyad homopolymers P5 and P5e and copolymers P[(5 and 5e)-co-6] both in solution and solid state (Figure S13 and S14). Excitation at λmax produced fluorescence spectra with noticeable polymer carbazole unit influence. Figure 1 illustrates the comparison of the solution (in THF) and solid state (spin cast from THF) photoluminescence (PL) spectra at designated excitations from Table 2. Dyad carbazole-functionalized homopolymers P5 and P5e and copolymers P[(5 and 5e)-co-6] influenced red-shifting in both the solution and as thin films. This observation appears to be consistent with extended conjugated systems (compare dicarbazole versus monocarbazole unit) that lower band-gaps facilitating long wavelength emission. Compared with absorption/fluorescence studies in solution and solid state where no noticeable N-substituted carbazole side-chain effects were observed, only the n-octyl substituted homopolymer P5a system showed significant emissive broadening as a thin film (Figure 1). This observation is presumably due to the alkyl side chains mitigating chain stacking thereby minimizing intrachain energy transfer and consequently promoting longer fluorescence lifetime via inter-chain energy transfer.

CONCLUSIONS

This work reports the synthesis, characterization, and properties of N-alkyl/aryl functionalized carbazole-functionalized semisiliconated poly(arylene ether)s. It expands the scope of employing fluorescence-containing polymers, specifically PFOB alkyl ethers, as feasible materials in organic-based electronics. The four step procedure for the preparation of high purity aryl TFVE end-capped carbazole monomers proved operationally simple, overall good isolated yields, and scaleable to multi-gram quantities. PFOB alkyl ether linkages by condensate-free thermal step-growth linear cyclodimerization of aryl TFVEs afforded optically clear, solution processable polymers with N-alkyl/aryl carbazole units intact. This metal-free, solventless polymerization methodology included the preparation of highly pure homo- and copolymers in very good yields as confirmed by selected analytical methods. The high thermal stability and solution processability of these amorphous systems makes them viable materials for preparing multilayered devices for OLED applications. Solution and thin film absorption/fluorescence spectroscopy revealed the main-chain carbazole units exhibit significant chromophore behavior in predominantly non-conjugated linear polymer systems. Their tailorable blue emission as thin films by way of N-aryl/aryl substitution is the focus of on-going investigation in order to determine electroluminescent properties as new candidates for hole-transport materials.

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ASSOCIATED CONTENT

Supporting Information
ATR-FTIR, NMR (1H, 13C, and 19F), DSC, TGA, and UV-Vis of monomers 5a-5e, homopolymers P5a-P5e and copolymers P[(5a-5e)-co-6] sequentially as Figures S1-S14. This material is available free of charge via the Internet at http://pubs.acs.org.

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Table 1. Selected Properties of Carbazole-PFCl Homopolymers and Copolymers

<table>
<thead>
<tr>
<th>Entry</th>
<th>% Mol Feed Ratio S5:S6</th>
<th>% Exp Ratio X:Y</th>
<th>GPC g mol$^{-1}$ Mw (POD)</th>
<th>$T_g/°C$</th>
<th>$T_d/°C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSA</td>
<td>100.0</td>
<td>100.0</td>
<td>12500 (2.2)</td>
<td>151</td>
<td>425</td>
</tr>
<tr>
<td>PSb</td>
<td>100.0</td>
<td>100.0</td>
<td>5800 (2.1)</td>
<td>—</td>
<td>453</td>
</tr>
<tr>
<td>PSc</td>
<td>100.0</td>
<td>100.0</td>
<td>4600 (2.0)</td>
<td>—</td>
<td>410</td>
</tr>
<tr>
<td>PSDb</td>
<td>100.0</td>
<td>100.0</td>
<td>5300 (1.5)</td>
<td>134</td>
<td>439</td>
</tr>
<tr>
<td>PSe</td>
<td>100.0</td>
<td>100.0</td>
<td>5100 (1.6)</td>
<td>157</td>
<td>446</td>
</tr>
<tr>
<td>P(Sa-co-6)</td>
<td>35.7:64.3</td>
<td>32.6:67.4</td>
<td>14400 (1.6)</td>
<td>150</td>
<td>444</td>
</tr>
<tr>
<td>P(Sb-co-6)</td>
<td>35.3:64.1</td>
<td>37.4:62.6</td>
<td>11600 (1.5)</td>
<td>—</td>
<td>460</td>
</tr>
<tr>
<td>P(Sc-co-6)</td>
<td>36.5:63.5</td>
<td>31.6:68.4</td>
<td>9600 (1.3)</td>
<td>—</td>
<td>435</td>
</tr>
<tr>
<td>P(Sd-co-6)</td>
<td>27.8:72.2</td>
<td>24.6:75.4</td>
<td>7200 (1.2)</td>
<td>—</td>
<td>461</td>
</tr>
<tr>
<td>P(Se-co-6)</td>
<td>26.72</td>
<td>38.2:61.8</td>
<td>9110 (1.9)</td>
<td>—</td>
<td>449</td>
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</table>


Table 2. Comparison of Solution and Thin Film Optical Properties of Carbazole-PFCl Homopolymers and Copolymers

<table>
<thead>
<tr>
<th>Entry</th>
<th>$\lambda_{abs}$ (nm$^{-1}$)</th>
<th>$\phi_{abs}$ (nm)</th>
<th>$\lambda_{PL}$ (nm)</th>
<th>$\phi_{PL}$ (nm)</th>
<th>$\Delta\varepsilon/\varepsilon_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSA</td>
<td>260 (300)</td>
<td>260 (300)</td>
<td>396, 376 (402, 426)</td>
<td>4.49 (3.52)</td>
<td>4.49 (3.52)</td>
</tr>
<tr>
<td>PSb</td>
<td>260 (300)</td>
<td>260 (300)</td>
<td>394, 376 (400, 382)</td>
<td>4.32 (3.69)</td>
<td>4.32 (3.69)</td>
</tr>
<tr>
<td>PSc</td>
<td>260 (300)</td>
<td>260 (300)</td>
<td>392, 373 (397, 379)</td>
<td>4.44 (3.72)</td>
<td>4.44 (3.72)</td>
</tr>
<tr>
<td>PSDb</td>
<td>310 (300)</td>
<td>310 (300)</td>
<td>418, 397 (425, 404)</td>
<td>4.52 (3.25)</td>
<td>4.52 (3.25)</td>
</tr>
<tr>
<td>PSe</td>
<td>301 (300)</td>
<td>301 (300)</td>
<td>413, 394 (420, 400)</td>
<td>4.44 (3.57)</td>
<td>4.44 (3.57)</td>
</tr>
<tr>
<td>P(Sa-co-6)</td>
<td>293 (300)</td>
<td>293 (300)</td>
<td>396, 376 (398, 390)</td>
<td>4.31 (3.46)</td>
<td>4.31 (3.46)</td>
</tr>
<tr>
<td>P(Sb-co-6)</td>
<td>260 (300)</td>
<td>260 (300)</td>
<td>392, 373 (395, 377)</td>
<td>4.32 (3.25)</td>
<td>4.32 (3.25)</td>
</tr>
<tr>
<td>P(Sc-co-6)</td>
<td>293 (300)</td>
<td>293 (300)</td>
<td>394, 376 (397, 380)</td>
<td>4.41 (3.69)</td>
<td>4.41 (3.69)</td>
</tr>
<tr>
<td>P(Sd-co-6)</td>
<td>310 (300)</td>
<td>310 (300)</td>
<td>418, 397 (422, 401)</td>
<td>4.25 (3.63)</td>
<td>4.25 (3.63)</td>
</tr>
<tr>
<td>P(Se-co-6)</td>
<td>301 (300)</td>
<td>301 (300)</td>
<td>413, 394 (416, 399)</td>
<td>4.49 (3.10)</td>
<td>4.49 (3.10)</td>
</tr>
</tbody>
</table>

$^b$: refers to the absorbance maximum for the $\pi-\pi^*$ transition. $^{(a)}$ Reported in nm based on $\lambda_{abs}$ excitation. $^{(c)}$ Estimated by onset of absorption.

Scheme 2. Synthetic procedure for the N-alkyl/aryl substituted carbazole-containing TFVE monomers.

Scheme 3. Synthetic procedure for the N-alkyl/aryl substituted carbazole containing PFCB aryl ether homo- and copolymers.

Figure 1. Solution in THF (top) and solid state (bottom) fluorescence spectra of PFCB aryl ether polymers and copolymers.