STAFF SUMMARY SHEET

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1	DFC	sig	VanValkenburg, O-6, 25Jan13	6			
2	DFER	approve	Kraus, Col 30Jan13	7		Actg Director Staff	
3	DFC	action		8			
4				9			
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SUMMARY

1. PURPOSE. To provide security and policy review on the document at Tab 1 prior to release to the public.

2. BACKGROUND.
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Title: Synthesis and Characterization of Blue Light Emissive Carbazole Containing Perfluorocyclobutyl Aryl Ether Polymers

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3. DISCUSSION. N/A

4. VIEWS OF OTHERS. N/A

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1 Tab
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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 purity confirmed by HRMS, NMR (^{1}H, ^{13}C, and ^{19}F), 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 pendent group or as a main chain member. The versatility to produce such homopolymers as well as copolymers provides access to novel electroluminescent 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 processibility.[10] Other partially fluorinated poly(aryl ether)s produced by chain extension of bisphenols with perfluorocycloolefins[11] and aryl TFVEs[12] have also demonstrated excellent solution processability and tailorability of the backbone for a multitude of applications. Specific to the scope of this work, semifluorinated poly(aryl ether)s 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.[13-15]

The preparation of the majority of functionalized poly(carbazole)s 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.[16-18] 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 photobleaching.[19] 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.[20-23] 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. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded on a JEOL Eclipse® 300 (300 MHz for ^{1}H, 75 MHz for ^{13}C, and 283 MHz for ^{19}F) in $CDCl_3$. Chemical shifts were reported in δ ppm with reference to internal tetramethylsilane (0 ppm), $CDCl_3$ (77 ppm), and $CFCl_3$ (0 ppm) for ^{1}H, ^{13}C and ^{19}F 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 (T_g) was obtained from a second heating cycle; the reported T_g values were taken at the midpoint of the C_p curve. Gel permeation chromatography (GPC) data were collected in $CHCl_3$ using polystyrene as a standard (Polymer Labs Easical 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 spectrofluorometer. Thin film absorption and emission data were collected on a Perkin-Elmer Lamda 950 spectrophotometer and Jobin-Yvon Fluorolog Tau-3 spectrofluorometer, respectively. Slit widths were kept constant for emission measurements.

General Methods and Materials. All reactions were carried out under nitrogen (passed over $CaSO_4$) 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(trifluorovinyloxy)benzene **6** was donated and also commercially available from

Tetramer Technologies, L.L.C. (Pendelton, SC) and distributed by Oakwood Chemicals, Inc. (Columbia, SC). 4,4,5,5-Tetramethyl-2-(4-trifluorovinyloxy-phenyl)-[1,3,2]dioxaborolane **4** was synthesized according to a procedure reported elsewhere[20] and is commercially available from Oakwood Chemicals, Inc. (Columbia, SC). HPLC grade tetrahydrofuran (THF) and diethyl ether (Et_2O) were dried and deoxygenated using a Pure-Solv solvent purification system from Innovative Technologies. Silica gel column chromatography was performed using Sorbent Silicagel (230-450 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 benzyltriethylammoniumchloride (0.8 g, 3.51 mmol) in toluene (100 mL) was added portion wise 50 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/triethylamine, 98/2 (v/v), R_f = 0.45) as a colorless viscous oil (29.6 g, 88%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.27 (d, *J* = 7.5 Hz, 2H), 7.61 (t, *J* = 7.5Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.39 (t, *J* = 7.5Hz, 2H), 4.35 (t, *J* = 7.2 Hz, 2H, $-NCH_2$), 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, $CDCl_3$): δ 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-iodotoluene (10.44 g, 47.3 mmol), KOH flakes (21.1g, 0.378 mol), CuCl (0.5 g, 5.05m), 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_4OH, and water, dried over anhydrous $MgSO_4$, and concentrated by rotary evaporation. The title compound was purified by column chromatography (SiO_2, hexanes/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 ($CDCl_3$, 300 MHz): δ 8.14 (d, *J* = 7.9 Hz, 2H), 7.43-7.39 (m, 8H), 7.29 (d, 2H), 2.49 (s, 3H, $-CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 141.1, 137.4, 135.2, 130.6, 127.1, 125.9, 123.3, 120.4, 119.8, 109.9, 21.4.

9-(4-Methoxyl)phenyl-carbazole (2c). The title compound was synthesized following the procedure for the preparation of **2b** using 4-iodoanisole affording white needle-like crystals (45%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 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, $CDCl_3$): δ 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 (12.4 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, concentrated by rotary evaporation. Purification by column chromatography (SiO_2, hexane/dichloromethane, 95/5 (v/v), R_f = 0.5) and crystallization (hexane/dichloromethane) yielded the title compound as white crystals (12.0 g, 76 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.10 (s, 2H), 7.55 (dd, *J* = 2Hz, 8.6 Hz, 2H), 7.23 (d, *J* = 8.6 Hz, 2H), 4.18 (t, *J* = 6.9 Hz, 2H, $-NCH_2-$), 1.83–1.78 (m, 2H), 1.29–1.23 (m, 10H), 0.83 (t, *J* = 6.9 Hz, 3H, $-CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 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 adaption from a previously reported procedure[24] following the preparation of **3a** affording white needle-like

crystals (9.4 g, 53%) by recrystallization from hexane/DCM mixture solvent. ^{1}H NMR ($CDCl_3$, 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, $-CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.2, 134.2, 130.8, 129.4, 126.9, 123.9, 113.0, 111.6, 21.4.

3,6-Dibromo-9-(4-methoxyl)phenyl-carbazole (3c). The title compound was synthesized following the procedure for the preparation of **3a** affording a white solid (85%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.13 (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, $-OCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): 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 (23.22 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 $MgSO_4$, filtered, and concentrated using rotary evaporation. The mixture was purified by column chromatography (SiO_2, hexane/dichloromethane/triethylamine, 75/24/1 (v/v/v), R_f = 0.35) and crystallization from hexane/dichloromethane) to afford the title compound as white crystals (2.59 g, 61 %). ^{1}H NMR ($CDCl_3$, 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); ^{13}C NMR ($CDCl_3$, 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 (SiO_2, hexane/dichloromethane/triethylamine, 60/39/1 (v/v/v), R_f = 0.35) and crystallization (hexane/dichloromethane) afforded white crystals (4.10 g, 50%). ^{1}H NMR ($CDCl_3$, 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, $-OCH_3$); ^{13}C NMR

(75 MHz, $CDCl_3$): 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 (SiO_2, hexane/dichloromethane, 90/10 (v/v), R_f = 0.35) and crystallization (hexane/dichloromethane) afforded a pale yellow solid (64%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.33 (d, 2H, *J* = 1.4 Hz), 8.30 (d, 2H, *J* = 2.1Hz), 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); ^{13}C NMR (75 MHz, $CDCl_3$): 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, 29.5, 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 (SiO_2, hexane/dichloromethane, 44/56 (v/v), R_f = 0.4) and crystallization (hexane/dichloromethane) afforded a white solid (74%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.37 (d, 2H, *J* = 1.4 Hz), 8.33 (d, 2H, *J* = 2.1Hz), 7.73 (dd, 2H, *J* = 1.7, 8.6Hz), 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), 7.38 (d, *J* = 8.6 Hz, 2H), 7.20 (d, *J* = 8.6 Hz, 2H), 7.11 (d, *J* = 8.9 Hz, 4H), 3.93 (s, $-OCH_3$, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 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, 55.7.

General Synthetic Procedure of Carbazole Aryl Trifluorovinyl Ether Monomers (5a–5e) *via* the Pd(0) Catalyzed Suzuki Coupling of 3a–3e with 4. Compounds **3a–3e** (5.0 mmol), **4** (3.18 g, 10.6 mmol), and 2M K_2CO_3 (17 mL) in THF (35 mL) was degassed with nitrogen. $Pd(PPh_3)_4$ (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 $MgSO_4$ and concentrated by rotary evaporation. The reaction mixture was further purified by chromatography (SiO_2, hexane/dichloromethane, 4/1 (v/v)) and recrystallized from hexane/dichloromethane to afford **5a–5e**.

3,6-Bis(4-(1,2,2-trifluorovinyloxy)phenyl)-9-octyl-9*H*-carbazole (5a). White powder (2.3 g, 73%); Mp 63 °C (DSC); ATR-FTIR (neat): υ 3043, 2930, 2854, 1830 (w, $CF=CF_2$), 1604, 1510, 1311 (st, br), 1165 (st, br), 833, 807 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): 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, $-NCH_2-$), 1.90–1.85(m, 2H), 1.36–1.24 (m, 10H), 0.84 (t, J = 6.9 Hz, 3H, $-CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.1, 140.5, 139.1, 131.4, 128.8, 125.4, 123.5, 118.9, 116.4, 109.3, 43.4, 31.9, 29.5, 29.3, 29.2, 27.4, 22.7, 14.2; ^{19}F NMR (283 MHz, $CDCl_3$): δ −119.7 (dd, *cis*-$CF=CF_2$, 2F, F_a), −126.5 (dd, *trans*-$CF=CF_2$, 2F, F_b), −133.4 (dd, $CF=CF_2$, 2F, F_c) (J_{ab} = 95.4 Hz, J_{ac} = 55.9 Hz, J_{bc} = 108.5 Hz); HRMS (FAB$^+$) Calculated (Found) for $C_{36}H_{31}O_2NF_6$ 623.22588 (623.22620).

3,6-Bis(4-(1,2,2-trifluorovinyloxy)phenyl)-9-*p*-tolyl-9*H*-carbazole (5b). White solid (1.7 g, 57%); Mp 94, 128 °C (DSC); ATR-FTIR (neat): υ 3040, 2929, 2855, 1831 (w, $CF=CF_2$), 1604, 1510, 1311 (st, br), 1166 (st, br), 835, 799 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): 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, 8.6 Hz, 2H), 7.42–7.49 (m, 6H), 7.20 (d, J = 8.3 Hz, 4H), 2.51(s, 3H, $-CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.2, 141.1, 139.0, 137.8, 134.9, 132.4, 130.7, 128.8, 126.9, 125.6, 123.9, 118.8, 116.4, 110.4, 21.4; ^{19}F NMR (283 MHz, $CDCl_3$): δ −119.7 (dd, *cis*-$CF=CF_2$, 2F, F_a), −126.5 (dd, *trans*-$CF=CF_2$, 2F, F_b), −133.4 (dd, $CF=CF_2$, 2F, F_c) (J_{ab} = 95.4 Hz, J_{ac} = 55.9 Hz, J_{bc} = 108.5 Hz); HRMS (FAB$^+$) Calculated (Found) for $C_{35}H_{21}O_2NF_6$ 601.14763 (601.14530).

3,6-Bis(4-(1,2,2-trifluorovinyloxy)phenyl)-9-(4-methoxyphenyl)-9*H*-carbazole (3c). White solid (2.2 g, 70%); Mp 60 °C (DSC); ATR-FTIR (neat): υ 3040, 2960, 2843, 1833 (w, $CF=CF_2$), 1604, 1510, 1311 (st, br), 1166 (st, br), 832, 802 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.34 (d, J = 1.7 Hz, 2H), 7.70 (dd, J = 2 Hz, 6.9 Hz, 2H), 7.60 (dd, J = 1.7 Hz, 8.6 Hz, 2H), 7.40 (d, J = 8.3 Hz, 4H), 7.38 (d, J = 8.3 Hz, 4H), 7.21(d J = 8.9 Hz, 2H), 7.13 (d, J = 8.9 Hz, 2H), 3.94 (s, 3H, $-OCH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.2, 154.4, 141.4, 139.0, 132.3, 130.1, 128.8, 128.5, 125.6, 123.8, 118.8, 116.4, 115.3, 110.3, 55.7; ^{19}F NMR (283 MHz, $CDCl_3$): δ −119.7 (dd, *cis*-$CF=CF_2$, 2F, F_a), −126.5 (dd, *trans*-$CF=CF_2$, 2F, F_b), −133.4 (dd, $CF=CF_2$, 2F, F_c) (J_{ab} = 95.4 Hz, J_{ac} = 55.9 Hz, J_{bc} = 108.5 Hz); HRMS (FAB$^+$) Calculated (Found) for $C_{35}H_{21}O_3NF_6$ 617.14255 (617.14270).

3-(4-(1,2,2-Trifluorovinyloxy)phenyl)-6-(3-(4-(1,2,2-trifluorovinyloxy)phenyl)-9-octyl-9*H*-carbazol-6-yl)-9-octyl-9*H*-carbazole (5d). White solid (3.21 g, 75%); Mp = 139 °C (DSC); ATR-FTIR (neat): υ 3040, 2924, 2852, 1830 (w, $CF=CF_2$), 1605, 1512, 1309 (st, br), 1168 (st, br), 834, 797 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.49 (s, 2H), 8.37 (s, 2H), 7.87 (d, J = 8.3 Hz, 2H), 7.72 (d, J = 8.6 Hz, 4H), 7.79 (d, J = 8.6 Hz, 2H), 7.50 (d, J = 8.6 Hz, 2H), 7.46 (d, J = 8.6 Hz, 2H), 7.21 (d, J = 8.9 Hz, 4H), 4.34 (t, J = 6.9 Hz, 4H), 1.96–1.89 (m, 4H), 1.43–1.29 (m, 20H), 0.89 (t, J = 7.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 154.4, 140.5, 140.2, 139.3, 133.5, 131.2, 128.8, 125.9, 125.1, 123.7, 123.6, 119.0, 118.9, 116.3, 109.2, 43.5, 31.9, 29.5, 29.3, 29.2, 27.5, 22.8, 14.2; ^{19}F NMR (283 MHz, $CDCl_3$): δ −119.7 (dd, *cis*-$CF=CF_2$, 2F, F_a), −126.5 (dd, *trans*-$CF=CF_2$, 2F, F_b), −133.4 (dd, $CF=CF_2$, 2F, F_c) (J_{ab} = 95.4 Hz, J_{ac} = 55.9 Hz, J_{bc} = 108.5 Hz); HRMS (FAB$^+$) Calculated (Found) for $C_{56}H_{54}O_2N_2F_6$ 900.40893 (900.40900).

3-(4-(1,2,2-Trifluorovinyloxy)phenyl)-6-(3-(4-(1,2,2-trifluorovinyloxy)phenyl)-9-(4-methoxyphenyl)-9*H*-carbazol-6-yl)-9-(4-methoxyphenyl)-9*H*-carbazole (5e)

White solid (3.9 g, 85%); Mp 135 °C (DSC); ATR-FTIR (neat): υ 3040, 2930, 2832, 1830 (w, $CF=CF_2$), 1603, 1510, 1311 (st, br), 1170 (st, br), 834, 804 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.50

(s, 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), 7.60 (dd, J = 1.7 Hz, J = 8.6 Hz, 2H), 7.51 (d, J = 8.6 Hz, 4H), 7.40 (dd, J = 1.7 Hz, 8.6 Hz, 4H), 7.21 (d, J = 8.6 Hz, 4H), 7.14 (dd, J = 1.7 Hz, 8.6 Hz, 4H), 3.95 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 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; ^{19}F NMR (283 MHz, $CDCl_3$) δ −119.7 (dd, *cis*-CF=CF_2, 2F, F_a), −126.5 (dd, *trans*-CF=CF_2, 2F, F_b), −133.4 (dd, CF=CF_2, 2F, F_c) (J_{ab} = 95.4 Hz, J_{ac} = 55.9 Hz, J_{bc} = 108.5 Hz); HRMS (FAB$^+$) Calculated (Found) for $C_{54}H_{34}O_4N_2F_6$ 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 > 85% yield.

P5a. ATR-FTIR (neat): υ 3050, 2925, 2850, 1603, 1510, 1311, 1170, 956 (cyclobutyl-F_6), 828, 801 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): 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, –NCH_2–), 1.85–1.75 (m, 2H), 1.34–1.21 (m, 10H), 0.81 (t, 3H, –CH_3); ^{19}F NMR (283 MHz, $CDCl_3$) δ trifluorovinyl endgroups at −118.9 (2F, dd, *cis*-CF=CF_2, F_a), −125.6 (2F, dd, *trans*-CF=CF_2, F_b), −134.1 (2F, dd, CF=CF_2, F_c) (J_{ab} = 95.4 Hz, J_{ac} = 59.2 Hz, J_{bc} = 108.5 Hz), 128.0–132.9 (m, cyclobutyl-F_6).

P5b. ATR-FTIR (neat): υ 3035, 2920, 1604, 1510, 1311, 1170, 955 (cyclobutyl-F_6), 836, 802 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): 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, -CH_3); ^{19}F NMR (282.8 MHz, $CDCl_3$): δ trifluorovinyl endgroups at

−119.5 (2F, dd, *cis*-CF=CF_2, F_a), −126.5 (2F, dd, *trans*-CF=CF_2, F_b), −133.4 (2F, dd, CF=CF_2, F_c) (J_{ab} = 95.4 Hz, J_{ac} = 59.2 Hz, J_{bc} = 108.5 Hz), broad at 128.0–132.9 (m, cyclobutyl-F_6).

P5c. ATR-FTIR (neat): υ 3037, 2836, 1604, 1510, 1311, 1170, 955 (cyclobutyl-F_6), 833, 801 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.26 (s, 2H), 7.52-7.62 (m, 6H, aromatic H), 7.06–7.39 (m, 10H, aromatic H), 3.87 (s, 3H, –OCH_3); ^{19}F NMR (283 MHz, $CDCl_3$) δ trifluorovinyl endgroups at −119.5 (2F, dd, *cis*-CF=CF_2, F_a), −126.5 (2F, dd, *trans*-CF=CF_2, F_b), −133.4 (2F, dd, CF=CF_2, F_c) (J_{ab} = 95.4 Hz, J_{ac} = 59.2 Hz, J_{bc} = 108.5 Hz), 128.0–132.8 (m, cyclobutyl-F_6).

P5d. ATR-FTIR (neat): υ 3046, 2920, 2850, 1604, 1510, 1311, 1170, 956 (cyclobutyl-F_6), 835, 796 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): ^{1}H NMR (300 MHz, $CDCl_3$): 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, –NCH_2–), 1.85–1.75 (m, 4H), 1.40–1.21 (m, 20H), 0.84 (t, 6H, –CH_3); ^{19}F NMR (282.8 MHz, $CDCl_3$): δ trifluorovinyl endgroups at −119.6 (2F, dd, *cis*-CF=CF_2, F_a), −126.5 (2F, dd, *trans*-CF=CF_2, F_b), −133.3 (2F, dd, CF=CF_2, F_c) (J_{ab} = 95.4 Hz, J_{ac} = 59.2 Hz, J_{bc} = 108.5 Hz), 127.9–132.8 (m, cyclobutyl-F_6).

P5e. ATR-FTIR (neat): υ 30370, 2830, 1604, 1510, 1311, 1170, 956 (cyclobutyl-F_6), 830, 801 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.31–8.38 (m, 4H), 7.04–7.69 (m, 24H, aromatic H), 3.84 (s, 6H, –OCH_3); ^{19}F NMR (283 MHz, $CDCl_3$): δ trifluorovinyl endgroups at −119.5 (2F, dd, *cis*-CF=CF_2, F_a), −126.5 (2F, dd, *trans*-CF=CF_2, F_b), −133.4 (2F, dd, CF=CF_2, F_c) (J_{ab} = 95.4 Hz, J_{ac} = 59.2 Hz, J_{bc} = 108.5 Hz), 128.0–132.8 (m, cyclobutyl-F_6).

P(5a-*co*-6). ATR-FTIR (neat): υ 3040, 2926 (st), 2855, 1603, 1510, 1311, 1170, 956 (cyclobutyl-F_6), 823, 803 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.22 (d), 7.14–7.61 (m, aromatic H), 4.28 (t, –NCH_2–), 1.85–1.75 (m), 1.31–1.21 (m), 0.81 (t, –CH_3); ^{19}F NMR (283 MHz, $CDCl_3$): δ trifluorovinyl endgroups at −118.9 (2F, dd, *cis*-CF=CF_2, F_a), −125.6 (2F, dd, *trans*-CF=CF_2, F_b), −134.1 (2F, dd, CF=CF_2, F_c) (J_{ab} = 95.4 Hz, J_{ac} = 59.2 Hz, J_{bc} = 108.5 Hz), 127.7–132.9 (m, cyclobutyl-F_6).

P(5b-*co*-6). ATR-FTIR (neat): υ 3040, 2840, 1607, 1513, 1311, 1170, 956 (cyclobutyl-F_6), 822, 806 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.29 (s), 7.16–7.62 (m, aromatic H), 2.47 (s, $-CH_3$); ^{19}F NMR (283 MHz, $CDCl_3$) δ trifluorovinyl endgroups at −119.3 (2F, dd, *cis*-$CF{=}CF_2$, F_a), −125.9 (2F, dd, *trans*-$CF{=}CF_2$, F_b), −133.7 (2F, dd, $CF{=}CF_2$, F_c) (J_{ab} = 95.4 Hz, J_{ac} = 59.2 Hz, J_{bc} = 108.5 Hz), 127.9–132.9 (m, cyclobutyl-F_6).

P(5c-*co*-6). ATR-FTIR (neat): υ 3043, 2840, 1605, 1510, 1310, 1170, 956 (cyclobutyl-F_6), 821, 807 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.29 (s), 7.16–7.61 (m, aromatic H), 3.89 (s, $-OCH_3$); ^{19}F NMR (283 MHz, $CDCl_3$) δ trifluorovinyl endgroups at −119.7 (2F, dd, *cis*-$CF{=}CF_2$, F_a), −125.9 (2F, dd, *trans*-$CF{=}CF_2$, F_b), −133.6 (2F, dd, $CF{=}CF_2$, F_c) (J_{ab} = 95.4 Hz, J_{ac} = 59.2 Hz, J_{bc} = 108.5 Hz), broad at 127.7–132.9 (m, cyclobutyl-F_6).

P(5d-*co*-6). ATR-FTIR (neat): υ 3040, 2930 (st), 2850, 1603, 1510, 1311, 1170, 955 (cyclobutyl-F_6), 827, 800 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.33 (d), 7.21–7.84 (m, aromatic H), 4.32 (t, $-NCH_2-$), 1.90–1.85 (m), 1.44–1.25 (m), 0.86 (t, $-CH_3$); ^{19}F NMR (283 MHz, $CDCl_3$) δ trifluorovinyl endgroups at −119.4 (2F, dd, *cis*-$CF{=}CF_2$, F_a), −125.9 (2F, dd, *trans*-$CF{=}CF_2$, F_b), −133.6 (2F, dd, $CF{=}CF_2$, F_c) (J_{ab} = 95.4 Hz, J_{ac} = 59.2 Hz, J_{bc} = 108.5 Hz), 127.8–132.9 (cyclobutyl-F_6).

P(5e-*co*-6). ATR-FTIR (neat): υ 3043, 2840, 1602, 1513, 1310, 1173, 956 (Cyclobutyl-F6), 827, 801 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 8.36 (d), 7.14–7.76 (m, aromatic H), 3.89 (s, $-OCH_3$); ^{19}F NMR (283 MHz, $CDCl_3$) δ trifluorovinyl endgroups at −119.7 (2F, dd, *cis*-$CF{=}CF_2$, F_a), −125.9 (2F, dd, *trans*-$CF{=}CF_2$, F_b), −133.6 (2F, dd, $CF{=}CF_2$, F_c) (J_{ab} = 95.4 Hz, J_{ac} = 59.2 Hz, J_{bc} = 108.5 Hz), 127.7–132.9 (cyclobutyl-F_6).

RESULTS & DISCUSSION

Aryl trifluorovinyl ether (TFVE) 3,6-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 *N*-alkyl/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 *N*-alkyl/arylated carbazoles **2a**–**2e** and at the 6,6′-position of dyads **2d** and **2e** upon treatment of **2a**–**2e** with *N*-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, ^{13}C, and ^{19}F NMR, FTIR, and HRMS.

PFCB aryl ether homopolymers **P5a**–**P5e** 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 (M_n) polymers based on GPC analysis. Homo- and copolymer molecular weights and their accompanying polydispersity indicies (PDI) are summarized in Table 1. Polymerization by the conversion of the aryl TFVE AMX pattern to the PFCB was observed by ^{19}F NMR (compare Figure S4 with Figure S7 or Figure S9). ^1H NMR functional group peak area integration confirmed incorporation of carbazole units in the homo- and copolymer 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 ($-CF{=}CF_2$) vibrational stretch ca. 1830 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 **P5b**–**P5e** produced oligomers with M_n

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 5 days resulted 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_n 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. ^1H 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[(5a–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 free-standing spin-cast films. Because they possess aryl TFVE groups, their latent thermal reactivity could lend 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. 230 °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

P5a 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 hompolymer **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 **P5d**, 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 **P5a** and **P(5a-*co*-6)** induce higher void volume, albeit the M_n of this series is slightly higher. Polymer degradation studies were performed using thermogravimetic 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 **P5a** 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 900 °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^{-4} 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 **P5a**–**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(aryl ether)s.[25-27] Onset excitation in solution was consistently lower for dyad homopolymers **P5d** and **P5e** and copolymers **P[(5d** and **5e)-*co*-6]** both in solution and solid state (Figure S13 and S14). Excitation at λ_{em} 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-functionalzed homopolymers **P5d** and **P5e** and copolymers **P[(5d** 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 intra-chain 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 semifluorinated poly(aryl ether)s. It expands the scope of employing fluorine-containing polymers, specifically PFCB aryl 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. PFCB aryl ether linkages by condensate-free thermal step-growth linear cyclodimerization of aryl TFVEs afforded optically-clear, solution processable polymers with *N*-alkyl/aryl carabzole 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 multi-layered devices for OLED applications. Solution and thin film absorption/fluorescence spectroscopy revealed the main-chain carbazole units exhibit inherent isolated chromorphore behavior in predominantly non-conjugated linear polymer system. Their tailorable blue emission as thin films by way of *N*-alkyl/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 (^{1}H, ^{13}C, and ^{19}F), 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-PFCB Homopolymers and Copolymers

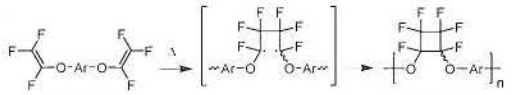
entry	% mol feed ratio **5x**:**6**[a]	% exp ratio x:y[b]	GPC/g mol^{-1}[c] M_n (PDI)	T_g/°C[d]	T_d/°C[e]
P5a	100:0	100:0	12500 (2.2)	151	425
P5b	100:0	100:0	5300 (2.1)	—	453
P5c	100:0	100:0	4600 (2.0)	—	410
P5d	100:0	100:0	5300 (1.5)	*134*[f]	439
P5e	100:0	100:0	5100 (1.6)	*157*[f]	446
P(5a-*co*-6)	35.7:64.3	32.6:67.4	14400 (1.6)	150	444
P(5b-*co*-6)	35.9:64.1	37.4:62.6	11600 (1.5)	—	460
P(5c-*co*-6)	36.5:63.5	31.6:68.4	9600 (1.3)	—	435
P(5d-*co*-6)	27.8:72.2	24.6:75.4	7200 (1.2)	—	461
P(5e-*co*-6)	28:72	38.2:61.8	9110 (1.3)	—	449

[a]Measured % mol ratio of monomers **5a**–**5e** and **6**. [d]Determined by ^{1}H NMR peak integration. [c]GPC in $CHCl_3$ using poly(styrene) as standard. [d]DSC (10 °C/min) in nitrogen determined by second heating cycle. [e]TGA onset (10 °C/min) of PFCB aryl ether chain extended polymers in nitrogen. [f]Very broad T_g.

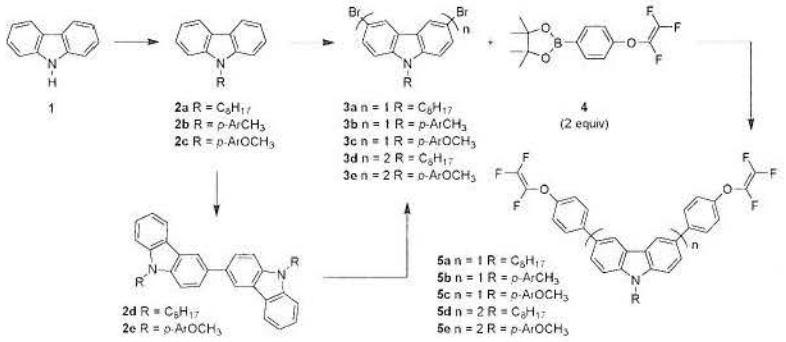
Table 2. Comparison of Solution and Thin Film Optical Properties of Carbazole-PFCB Homopolymers and Copolymers

entry	abs λ_{max}/nm[a] THF (film)	PL λ_{max}/nm[b] THF (film)	ΔE/eV[c] THF (film)
P5a	293 (260, 300)	396, 376 (402, 426)	4.49 (3.52)
P5b	293 (263, 297)	394, 376 (400, 382)	4.32 (3.69)
P5c	296 (260, 297)	392, 373 (397, 379)	4.44 (3.72)
P5d	310 (261, 320)	418, 397 (425, 404)	4.52 (3.26)
P5e	301 (260, 306)	413, 394 (420, 400)	4.44 (3.57)
P(5a-*co*-6)	293 (260, 300)	396, 376 (398, 380)	4.31 (3.46)
P(5b-*co*-6)	296 (269, 312)	392, 373 (395, 377)	4.32 (3.26)
P(5c-*co*-6)	293 (263, 297)	394, 376 (397, 380)	4.41 (3.69)
P(5d-*co*-6)	310 (263, 317)	418, 397 (422, 401)	4.25 (3.63)
P(5e-*co*-6)	301 (260, 310)	413, 394 (418, 399)	4.49 (3.19)

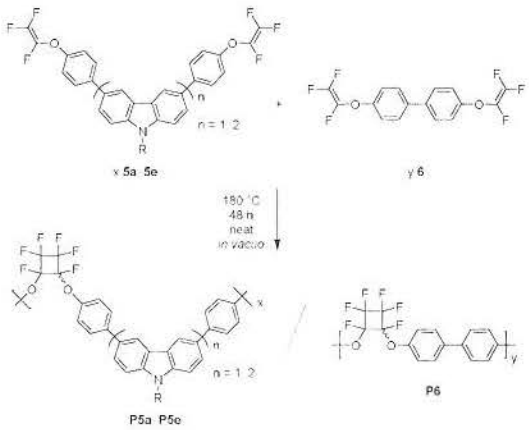
[a]λ refers to the absorbance maximum for the π–π^* transition. [b]λ_{max} reported in nm based on λ_{max} excitation. [c]Estimated by onset of absorption.



Scheme 1. Step-growth thermal [2 + 2] cyclodimerizaton of aryl TFVE monomers to amorphous PFCB aryl ether polymers.



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.

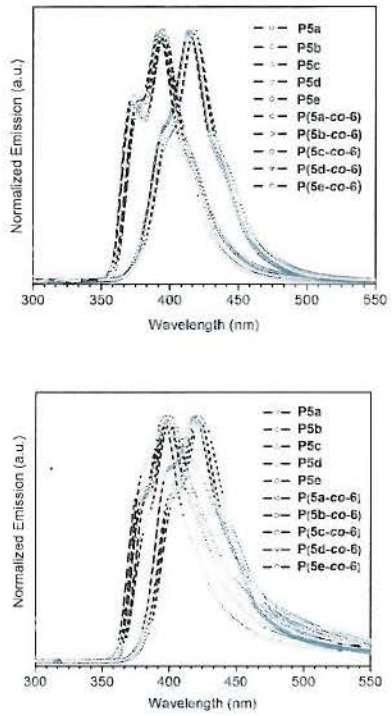


Figure 1. Solution in THF (top) and solid state (bottom) fluorescence spectra of PFCB aryl ether polymers and copolymers.