Modular Approach to Chromophore Encapsulation in Fluorinated Arylene Vinylene Ether Polymers Possessing Tunable Photoluminescence

Scott T. Iacono,[†] Stephen M. Budy,[‡] Justin D. Moody, Rhett C. Smith, and Dennis W. Smith, Jr.*

Department of Chemistry, School of Material Science and Engineering, and Center for Optical Materials Science and Engineering Technologies (COMSET), Clemson University, Clemson, South Carolina 29634

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ABSTRACT: New fluorinated arylene vinylene ether (FAVE) polymers were prepared by a facile, metal-free condensation polymerization of fluorene, phenylenevinylene, dithiophene, or thiadiazole chromophore-containing bisphenols with bis(trifluorovinyloxy)biphenyl. The addition of chromophores encapsulated into the polymers were prepared in good yields and characterized by ^{1}H and ^{19}F NMR and GPC. Thermal analysis by differential scanning calorimetry (DSC) confirmed the polymers are entirely amorphous and are easy to solution process, producing optically transparent, flexible films. Thermal gravimetric analysis (TGA) showed they possess high thermal stability with decomposition temperatures of 340−387 °C and 308−443 °C in nitrogen and air, respectively. Chromophore inclusion was confirmed by ultraviolet−visible (UV−vis) spectroscopy, which demonstrated tailorable photoluminescence (PL) in both the solution and the solid state by selective substitution of the chromophore. Polymer thin film PL studies revealed notable red-shifts compared with polymer solutions presumably attributable to aggregation in the solid state. Solution quantum yields of the polymers were comparable to those reported for the single chromophores used in this study.

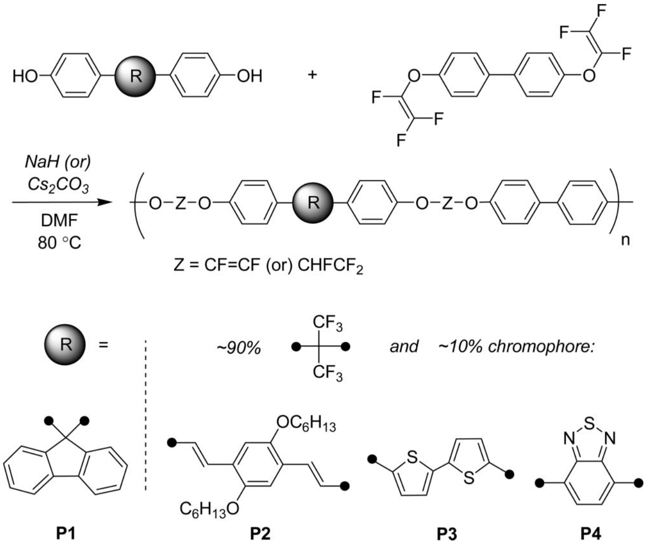
Introduction

The discovery of the first electrically conducting polyacetylenes[1] has led to a renaissance of utilizing light emissive organic conjugated polymers for the commercial preparation of highly efficient light emitting devices, magnetic storage media, photovoltaics, electro-optics, and chemical sensors.[2] However, the rigid nature of many conjugated oligomers or conjugated polymer (CP) systems renders them insoluble, thus requiring costly vacuum deposition, lithographic templating, or other labor-intensive processing for device fabrication. Although there are notable examples of soluble CP systems, they require multistep monomer preparation and often employ expensive transition metal catalysts for their polymerization.[3] Consequently, residual transition metals affect device optoelectronic properties and efficiency, confounding interpretation of data, comparison to related systems, and reproducibility.[4] For these reasons, there remains a need for easily prepared, solution processable, and transition metal-free polymers capable of efficient light emission.

Nucleophilic addition of alcohols to perfluorinated olefins is a well established transformation in organofluorine chemistry.[5] This methodology has led to an alternate preparation of perfluorinated polyethers (PFPE),[6] an important class of elastomers that display ultralow surface friction, resistance to creep, and excellent thermal and chemical resistance.[7] While fluoropolymers possess these superior benefits over their hydrogen-containing analogs, they have shown little utility for light emissive applications. This is primarily due to poor solution processability because of their high crystalline nature and their lack of extended $\pi-\pi$ conjugation. It has been shown; however, that introducing fluorine into conjugated polymers diminishes their susceptibility to light-induced oxidation, thus improving their resistance to photobleaching.[8]

We have recently developed a transition metal-free, step-growth polymerization of commercial bisphenols (1) and bis(trifluorovinyloxy)biphenyl (2) affording telechelic and cross-linkable fluorinated arylene vinylene ether (FAVE) polymers enriched with a 1,2-difluorovinylene (Z = CF=CF) or hydro-1,2,2-fluoroethane (Z = $CHFCF_2$) in the backbone (Scheme 1).[9] Bis(trifluorovinyloxy)biphenols are well-known to undergo thermal [2 + 2] cyclopolymerization[10] to afford a class of amorphous, processable perfluorocyclobutyl (PFCB) aryl ether polymers for a multitude of high performance materials.[11] Specifically, FAVE polymers also exhibit high thermal stability and produce flexible, optically transparent films by simple spin-

Scheme 1. Step-Growth Polymerization of Chromophore Containing Bisphenols and Bis(trifluorovinyloxy)biphenyl[a]



[a] **P2**−**P4** are copolymers containing 6F bisphenol A (R = $C(CF_3)_2$). Percentages shown in the caption for **P2**−**P4** are represented as mol %.

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* To whom correspondence should be addressed. E-mail: dwsmith@clemson.edu.

[†] Current Address: U.S. Air Force, Patrick Air Force Base, FL 32925.

[‡] Current Address: Department of Chemistry, University of Arizona, Tucson, AZ 85721.

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or drop-casting. Since this original report, we have discovered that these unique polymers exhibit unanticipated visible photoluminescence with or without enchainment of known visible light emitting groups. Nonconjugated polymer matrices have been used extensively to either blend or covalently attach single molecules[12] or conjugated segments.[13] In many cases, such systems have been shown to minimize undesired fluorescence/phosphorescence exciton quenching often exhibited by fully CP systems.[14] Such materials would complement existing materials in photonic applications such as polymer light emitting diodes (PLEDs), chemical sensing, and photovoltaics (PVs). Herein, we describe the synthesis, characterization, and optical properties of new FAVE polymers with tailorable photoemission depending on the simple bisphenol chromophore chosen. Our modular approach yielded polymers with enchained chromophore segments capable of highly efficient, tunable photoluminescence.

Experimental Section

General Procedures. All reagents and solvents were purified according to established procedures unless otherwise noted.[15] All reactions and solvent transfers were carried out under an atmosphere of nitrogen or in a glovebox. Flasks and syringes were flamed-dried under vacuum and allowed to cool in a desiccator prior to use. Solid films of **P1**−**P4** were prepared by spin casting the polymer solutions in THF onto quartz slides at 2500−3000 RPM using a Chemat KW-4A spin coater. Polymer film thicknesses were on average about 150−200 nm, as measured by an Alpha-Step 200 Profiler profilometer.

Materials. 4,4′-(9-Fluorenylidene)diphenol (used for polymer **P1** and **P1′**) and 2,2-bis(4-hydroxyphenyl)hexafluoropropane (used for polymers **P2**−**P4**) were purchased from Aldrich. 2,2-Bis(4-hydroxyphenyl)hexafluoropropane (6F bisphenol A, 1) was donated by The Dow Chemical Company. 4,4′-Bis(4-trifluorovinyloxy)biphenyl (2) was donated and is commercially available from Tetramer Technologies, LLC and distributed though Oakwood Chemicals, Inc. Deionized water used for quantum yield determination (Φ_F) was degassed prior to optical measurements. HPLC grade THF (Aldrich) and reagent grade Et_2O (Aldrich) were dried and deoxygenated by passage through a Pure-Solv solvent purification system equipped with Cu/Al columns from Innovative Technologies. Anhydrous DMF was further dried by storage over anhydrous $MgSO_4$ under a nitrogen atmosphere. All other reagents and solvents were purchased from Aldrich.

Instrumentation. ^{1}H, ^{13}C, and ^{19}F NMR data were obtained on a JEOL Eclipse^{+} 300 and chemical shifts were reported in part per million (δ ppm). ^{1}H NMR was internally referenced to tetramethylsilane (δ 0.0), ^{13}C NMR chemical shifts were reported relative to the center peak of the multiplet for $CDCl_3$ (δ 77.0 (t)), and ^{19}F NMR was referenced to $CFCl_3$.

Gel permeation chromatography (GPC) data were collected using polystyrene as a standard (Polymer Laboratories Easical PS-2) using a Waters 2695 Alliance System with UV−vis detection for samples in $CHCl_3$ or a Waters 515 HPLC pump coupled with a Waters 2414 refractive index detector for samples in THF. GPC samples were eluted in series through Polymer Laboratories PLGel 5 mm Mixed-D and Mixed-E columns at 35 °C.

Differential scanning calorimetry (DSC) analysis and thermal gravimetric analysis (TGA) were performed on a TA Q1000 instrument and TA Hi-Res TGA2950 instrument, respectively.

Absorbance and emission data for quantum yields (Φ_F) 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.

1,4-Bis(*p*-hydroxystyryl)-2,5-dihexyloxybenzene (used for polymer P2). The title compound was prepared using a modified literature procedure and NMR data agreed with previously published work.[16] Potassium *tert*-butoxide (180 mg, 1.61 mmol) in THF (10 mL) was added dropwise to a stirred solution of 1,4-bis(diethoxyphosphinylmethyl)-2,5-di-*n*-hexyloxybenzene[17] (424 mg, 0.74 mmol) and 4-(*tert*-butyldimethylsiloxy)benzaldehyde[18] (380 mg, 1.61 mmol) dissolved in THF (50 mL) at room temperature. After 12 h, the reaction mixture was poured into an equal volume of 10% methanolic HCl. Deionized water (50 mL) and Et_2O (100 mL) were added, then the fluorescent yellow organic layer was collected, washed with deionized water (2 × 50 mL) and brine (50 mL), and concentrated under vacuum. The crude product was dissolved in THF (10 mL) and deprotected by treatment with TBAF (20 mL, 1 M in THF). After 6 h, CH_2Cl_2 (20 mL) and deionized water (20 mL) were added, then the organic layer was collected and the aqueous layer was extracted with CH_2Cl_2 (2 × 50 mL). Combined organic layers were washed with deionized water (2 × 50 mL), dried over Na_2SO_4, filtered, and concentrated under vacuum. Purification of the residue by flash chromatography on silica gel 60 with 1:1 (v/v) ethyl acetate/hexanes as eluent afforded the title compound as a yellow solid (120 mg, 32%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.44 (d, J = 8.4 Hz, 4H), 7.32 (d, J = 16.2 Hz, 2H), 7.11 and 7.05 (s, 3.9:1 (*Z*)/(*E*)-vinyl, 4H), 6.84 (d, J = 8.7 Hz, 4H), 4.76 (s, 2H), 4.60 (t, J = 6.6 Hz, 4H), 1.89 (pentet, J = 6.6 Hz, 4H), 1.61−1.34 (m, 12H), 0.94 (t, J = 6.9 Hz, 6H); ^{13}C NMR ($CDCl_3$, 76 MHz) δ 155.1, 151.0, 131.1, 128.1, 128.0, 126.9, 121.6, 115.7, 110.6, 69.8, 31.7, 29.6, 26.0, 22.8, 14.1.

5,5′-Bis(4-hydroxyphenyl)-2,2′-bithiophene (used for P3 and P3′). The title compound was prepared using a modified procedure and NMR data agreed with previously published work.[19] 5,5′-Dibromo-2,2′-bithiophene (1.94 g, 6.00 mmol), 4-hydroxyphenylboronic acid (1.69 mg, 12.24 mmol), Na_2CO_3 (30 mL, 2 M), and DMF (30 mL) were charged in a round-bottom flask. The reaction mixture was sparged with N_2 for 10 min. $Pd(PPh_3)_4$ (692 mg, 0.60 mmol) was then added and the reaction mixture was placed in a preheated oil bath at 100 °C for 24 h. The reaction mixture was allowed to cool to room temperature and the precipitated solids were collected by filtration. Recrystallization from hot DMSO (ca. 90 °C) afforded the title compound as a pale green solid (850 mg, 40%). ^{1}H NMR (DMSO-d_6, 300 MHz) δ 9.69 (s, br, 2H), 7.43 (d, J = 8.5 Hz, 4H), 7.24 and 7.20 (AB pattern, J = 3.78 Hz, 4H), 7.77 (d, J = 5.6 Hz, 4H); ^{13}C NMR (DMSO-d_6, 76 MHz) δ 157.9, 143.1, 134.7, 127.2, 125.2, 125.0, 123.3, 116.4.

4,4′-(2,1,3-Benzothiadiazole-4,7-diyl)bisphenol (used for polymer P4). The title compound was prepared in two steps. First step: bromine (11.3 g, 220 mmol) was added dropwise over a 1 h period to a refluxing solution of 1,2,3-benzothiadiazole (10 g, 73.4 mmol) in HBr (47 wt %). The solution was allowed to reflux for an additional 2 h after bromine addition. The *hot* solution was vacuum filtered and the solid was washed repeatedly with deionized H_2O (5−10 × 200 mL). The solid was then dissolved in $CHCl_3$ with activated carbon (5 g) and heated to reflux. After 1 h, the solution was filtered and concentrated in vacuum. The solid was recrystallized from 1:4 (v/v) $CHCl_3$/hexanes to afford the title compound as silver-gray needles (12.6 g, 58%).

Second step: 4,7-bibromo-2,1,3-benzothiadiazole (1.0 g, 3.40 mmol), 4-hydroxyphenylboronic acid (961 mg, 6.97 mmol), Na_2CO_3 (17 mL, 2 M), and DMF (17 mL) were charged in a round-bottom flask. The reaction mixture was sparged with N_2 for 10 min. $Pd(PPh_3)_4$ (393 mg, 0.34 mmol) was then added and the reaction mixture was placed in a preheated oil bath at 100 °C for 24 h. $CHCl_3$ was added after the solution was cooled to room temperature. The organic layer was separated and the aqueous layer was extracted with $CHCl_3$ (2 × 20 mL). Combined organic layers were washed with deionized water (4 × 50 mL), dried ($MgSO_4$), filtered, and concentrated under vacuum. The solid was recrystallized from 1:5 (v/v) $CHCl_3$/hexanes at 0 °C to afford the title compound as a brown solid (580 mg, 54%). ^{1}H NMR (DMSO-d_6, 300 MHz) δ 9.69 (s, br, 2H), 7.84−7.76 (s, 6H), 6.90 (d, J = 8.25 Hz, 4H); ^{13}C NMR (DMSO-d_6, 76 MHz) δ 158.3, 154.0, 131.8, 130.8, 128.3, 127.6, 115.9.

Preparation of Polymer P1. A solution of 4,4′-(9-fluorenylidene)diphenol (441 mg, 1.26 mmol) dissolved in anhydrous DMF (2 mL) were added dropwise to a stirred suspension of NaH

(2.20 mmol) in DMF (2 mL) at room temperature for 1 h. 4,4′-Bis(4-trifluorovinyloxy)biphenyl (2; 436 mg, 1.26 mmol) in DMF (2 mL) was transferred into the solution via syringe in a single portion. The solution was then placed in a preheated oil bath at 80 °C. After 4 h, the solution contents were then precipitated into H_2O, filtered under vacuum, and washed sequentially with deionized H_2O, MeOH, and hexanes. The solid polymer was dried in a vacuum oven at 60 °C for 24 h. Additional purification was performed by dissolving the dried polymer in a minimal amount of THF and precipitated in deionized water, filtered, and washed sequentially with MeOH and hexanes. The solid polymer was then dried in a vacuum oven at 60 °C for an additional 24 h to afford **P1** as a white fibrous solid (760 mg, 87%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.80−8.78 (m), 7.37−6.85 (m), 5.88 (broad dt, J = 59.4 Hz, C*H*FCF$_2$); ^{19}F NMR ($CDCl_3$, 283 MHz) δ −85.7 (d, J = 146.1 Hz, CHFCF_2), −119.3 (dd, J = 57.4, 95.5 Hz, residual (*cis*)-CF═CF_2), −121.5 (d, J = 32.9 Hz, (*Z*)-CF═CF), −122.0 (d, J = 39.4 Hz, (*E*)-CF═CF), −126.3 (dd, J = 98.7, 111.8 Hz, residual (*trans*)-CF═CF_2), −127.8 (s, br, (*Z*)-CF═CF), −133.7 (dd, J = 55.9, 108.6 Hz, residual C*F*═CF$_2$), −138.6 (d, J = 59.3 Hz, CH*F*CF$_2$). GPC in $CHCl_3$ relative to polystyrene gave a monomodal distribution of M_n = 17300 ($M_\mathrm{w}/M_\mathrm{n}$ = 2.4). DSC analysis of second heating at 10 °C/min to 200 °C gave T_g = 150 °C and TGA (10 °C/min) gave T_d (onset) = 340 °C in nitrogen and 320 °C in air.

Preparation of Polymers P1′ A suspension of 4,4′-(9-fluorenylidene)diphenol (882 mg, 2.51 mmol), 4,4′-bis(4-trifluorovinyloxy)biphenyl (872 mg, 2.51 mmol), and Cs_2CO_3 (410 mg, 1.26 mmol) in a minimal amount of DMF to initiate stirring were heated to 80 °C for 24 h. After 4 h, the solution contents were then precipitated into H_2O, filtered under vacuum, and washed sequentially with deionized H_2O, MeOH, and hexanes. The solid polymer was dried in a vacuum oven at 60 °C for 24 h. Additional purification was performed by dissolving the dried polymer in a minimal amount of THF and precipitated in deionized water, filtered, and washed sequentially with MeOH and hexanes. The solid polymer was then dried in a vacuum oven at 60 °C for an additional 24 h to afford **P1′** as a white fibrous solid (920 mg, 52%). ^{19}F NMR ($CDCl_3$, 283 MHz) δ −85.6 and −86.1 (AB pattern, J = 148.1 Hz, CHFCF_2), −121.5 and −122.2 (d, J = 35.8 Hz, residual (*Z*)-CF═CF), −127.8 (s, residual (*E*)-CF═CF), −138.6 (d, J = 59.2 Hz, CH*F*CF$_2$). GPC in $CHCl_3$ relative to polystyrene gave a monomodal distribution of M_n = 10500 ($M_\mathrm{w}/M_\mathrm{n}$ = 1.8). DSC analysis of second heating at 10 °C/min to 200 °C gave T_g = 155 °C and TGA (10 °C/min) gave T_d (onset) = 357 °C in nitrogen and 355 °C in air.

Preparation of Polymer P2. A solution of 1,4-bis(*p*-hydroxystyryl)-2,5-dihexyloxybenzene (50 mg, 0.23 mmol) and 2,2-bis(4-hydroxyphenyl)hexafluoropropane (696 mg, 2.07 mmol) dissolved in anhydrous DMF (2 mL) were added dropwise to a stirred suspension of NaH (222 mg, 9.24 mmol) in DMF (2 mL) at room temperature for 1 h. 4,4′-Bis(4-trifluorovinyloxy)biphenyl (2; 800 mg, 2.30 mmol) in DMF (2 mL) was transferred into the solution via syringe in a single portion. The solution was then placed in a preheated oil bath at 80 °C. After 4 h, the solution contents were then precipitated into H_2O, filtered under vacuum, and washed sequentially with deionized H_2O, MeOH, and hexanes. The solid polymer was dried in a vacuum oven at 60 °C for 24 h. Additional purification was performed by dissolving the dried polymer in a minimal amount of THF and precipitated in deionized water, filtered, and washed sequentially with MeOH and hexanes. The solid polymer was then dried in a vacuum oven at 60 °C for an additional 24 h to afford **P2** as a yellow fibrous solid (900 mg, 58%). ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.89−6.90 (m), 6.91 (broad dt, J = 57.0 Hz, C*H*FCF$_2$), 4.06−3.99 (m, -OCH$_2$-), 1.89−1.79 (m, -CH$_2$-), 1.55−1.22 (m, -CH$_2$-), 0.97−0.81 (m, -CH$_3$); ^{19}F NMR (DMSO-d_6, 283 MHz) δ −63.4 (s, C(CF_3)$_2$), −85.3 and −86.4 (AB pattern, J = 141.7 Hz, CHFCF_2), −120.7 and −122.2 (d, J = 42.7 Hz, (*Z*)-CF═CF), −126.6 and −128.6 (d, J = 111.8 Hz, (*E*)-CF═CF), −138.5 (d, J = 59.2 Hz, CH*F*CF$_2$). GPC in THF relative to polystyrene gave a monomodal distribution of M_n = 27700 ($M_\mathrm{w}/M_\mathrm{n}$ = 1.8). DSC analysis of second heating at 10 °C/min to 200 °C gave T_g = 98 °C and TGA (10 °C/min) gave T_d (onset) = 325 °C in nitrogen and 318 °C in air.

Preparation of Polymer P3. A solution of 5,5′-bis(4-hydroxyphenyl)-2,2′-bithiophene (49 mg, 0.14 mmol), 2,2-bis(4-hydroxyphenyl)hexafluoropropane (437 mg, 1.30 mmol), and 4,4′-bis(4-trifluorovinyloxy)biphenyl (500 mg, 1.44 mmol) were used following the procedure outlined for the preparation of **P2** *except excess NaH* (1.72 mg, 7.2 mmol) was used to afford **P3** as a green fibrous solid (585 mg, 60%). ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.70−7.18 (m), 6.68 (broad dt, J = 57.7 Hz, C*H*FCF$_2$); ^{19}F NMR (DMSO-d_6, 283 MHz) δ −63.4 (s, C(CF_3)$_2$), −85.2 and −86.4 (AB pattern, J = 141.5 Hz, CHFCF_2), −120.7 and −122.0 (d, J = 39.5 Hz, (*Z*)-CF═CF), −127.2 and −129.2 (d, J = 108.6 Hz, (*E*)-CF═CF), −141.1 (d, J = 55.9 Hz, CH*F*CF$_2$). GPC in THF relative to polystyrene gave a monomodal distribution of M_n = 12200 ($M_\mathrm{w}/M_\mathrm{n}$ = 1.5). DSC analysis of second heating at 10 °C/min to 200 °C gave T_g = 102 °C and TGA (10 °C/min) gave T_d (onset) = 352 °C in nitrogen and 328 °C in air.

Preparation of Polymer P3′ A solution of 5,5′-bis(4-hydroxyphenyl)-2,2′-bithiophene (101 mg, 0.29 mmol), 2,2-bis(4-hydroxyphenyl)hexafluoropropane (877 mg, 2.61 mmol), and 4,4′-bis(4-trifluorovinyloxy)biphenyl (1.0 g, 2.90 mmol) were used following the procedure outlined for the preparation of **P2** to afford **P3** as a pale green fibrous solid (1.20 g, 61%). ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.70−7.18 (m), 6.68 (broad dt, J = 57.7 Hz, C*H*FCF$_2$); ^{19}F NMR (DMSO-d_6, 283 MHz) δ −63.4 (s, C(CF_3)$_2$), −85.3 and −86.4 (AB pattern, J = 141.5 Hz, CHFCF_2), −120.7 and −122.0 (d, J = 39.5 Hz, (*E*)-CF═CF), −127.2 and −129.2 (d, J = 108.6 Hz, (*E*)-CF═CF), −141.1 (d, J = 55.9 Hz, CH*F*CF$_2$). GPC in $CHCl_3$ relative to polystyrene gave a monomodal distribution of M_n = 10200 ($M_\mathrm{w}/M_\mathrm{n}$ = 2.1). DSC analysis of second heating at 10 °C/min to 200 °C gave T_g = 104 °C and TGA (10 °C/min) gave T_d (onset) = 341 °C in nitrogen and 395 °C in air.

Preparation of Polymer P3″ A solution of 5,5′-bis(4-hydroxyphenyl)2,2′-bithiophene (50 mg, 0.14 mmol), 2,2-bis(4-hydroxyphenyl)hexafluoropropane (437 mg, 1.30 mmol), 4,4′-bis(4-trifluorovinyloxy)biphenyl (500 mg, 1.44 mmol), and Cs_2CO_3 (235 mg, 0.50 mmol) in a minimal amount of DMF to initiate stirring were heated to 80 °C for 24 h. After 4 h, the solution contents were then precipitated into H_2O, filtered under vacuum, and washed sequentially with deionized H_2O, MeOH, and hexanes. The solid polymer was dried in a vacuum oven at 60 °C for 24 h. Additional purification was performed by dissolving the dried polymer in a minimal amount of THF and precipitated in deionized water, filtered, and washed sequentially with MeOH and hexanes. The solid polymer was then dried in a vacuum oven at 60 °C for an additional 24 h to afford **P3′** as a green fibrous solid (520 mg, 53%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.75−7.10 (m), 5.94 (broad dt, J = 57.7 Hz, C*H*FCF$_2$); ^{19}F NMR ($CDCl_3$, 283 MHz) δ −63.8 (s, C(CF_3)$_2$), −85.2 and −86.3 (AB pattern, J = 161.2 Hz, CHFCF_2), −120.8 and −122.1 (d, J = 42.8 Hz, residual (*Z*)-CF═CF), −126.7 and −128.5 (d, J = 111.7 Hz, residual (*E*)-CF═CF), −138.5 (d, J = 59.2 Hz, CH*F*CF$_2$). GPC in $CHCl_3$ relative to polystyrene gave a monomodal distribution of M_n = 36100 ($M_\mathrm{w}/M_\mathrm{n}$ = 2.6). DSC analysis of second heating at 10 °C/min to 200 °C gave T_g = 90 °C and TGA (10 °C/min) gave T_d (onset) = 387 °C in nitrogen and 443 °C in air.

Preparation of Polymer P4. Monomers 4,4′-(2,1,3-benzothiadiazole-4,7-diyl)bisphenol (45 mg, 0.14 mmol), 2,2-bis(4-hydroxyphenyl)hexafluoropropane (437 mg, 1.30 mmol), and 4,4′-bis(4-trifluorovinyloxy)biphenyl (500 mg, 1.44 mmol) were used following the procedure outlined for the preparation of **P2** to afford **P4** as a green fibrous solid (600 mg, 61%). ^{1}H NMR (DMSO-d_6, 300 MHz) δ 7.80−7.10 (m), 6.68 (broad dt, J = 59.1 Hz, C*H*FCF$_2$); ^{19}F NMR (DMSO-d_6, 283 MHz) δ −63.5 (s, C(CF_3)$_2$), −85.7 and −86.2 (AB pattern, J = 140.0 Hz, CHFCF_2), −120.8 and −122.0 (d, J = 42.7 Hz, (*Z*)-CF═CF), −127.3 and −129.2 (d, J = 111.8 Hz, (*E*)-CF═CF), −141.2 (d, J = 55.9 Hz, CH*F*CF$_2$). GPC in $CHCl_3$ relative to polystyrene gave a monomodal distribution of M_n = 15200 ($M_\mathrm{w}/M_\mathrm{n}$ = 1.8). DSC analysis of second heating at 10 °C/

Table 1. Selected Physical Properties of Polymers P1−P4

entry	$M_n \times 10^{-3}$GPC	M_w/M_n	% Z = CF═CF[a]	T_g[b] (°C)	T_d (°C) N_2 (air)[c]
P1	17.3[d]	2.4	80	150	340 (320)
P1′	10.5[d]	1.8	22	155	357 (355)
P2	27.7[e]	1.8	68	98	325 (318)
P3	12.2[e]	1.5	83	102	352 (328)
P3′	10.2[d]	2.1	52	104	341 (395)
P3″	36.1[d]	2.6	7	90	387 (443)
P4	15.2[d]	2.8	70	64	368 (358)

[a] Determined by ^{19}F NMR peak integration; about 1.2:1 (*Z*)/(*E*) isomers. [b] DSC (10 °C/min) in argon, second heating. [c] TGA onset at 10 °C/min. [d] GPC in $CHCl_3$ using polystyrene standards. [e] GPC in THF using polystyrene standards.

min to 200 °C gave T_g = 64 °C and TGA (10 °C/min) gave T_d (onset) = 368 °C in nitrogen and 358 °C in air.

Results and Discussion

Polymer Synthesis and Characterization. The highest achieved degree of polymerization to yield polymers **P1**−**P4** (Scheme 1) involved generation of the bisphenoxide sodium salt of 1 using NaH in DMF, followed by addition of aryl TFVE (1 equiv) and heating at 80 °C for 4 h. Initial attempts at polymerization of aryl TFVE with phenylenevinylene-, dithiophene-, or thiadiazole-functionalized bisphenols produced low molecular weight oligomers probably due to their insolubility. Introduction of the partially fluorinated and flexible bisphenol 2,2-bis(4-hydroxyphenyl)hexafluoropropane (i.e., 6F bisphenol A or R = $C(CF_3)_2$ in Scheme 1) as a solubilizing segment afforded high molecular weight copolymers **P2**−**P4** that are soluble in common organic solvents such as THF, $CHCl_3$, DMSO, and cyclopentanone. The optimum molecular weight of polymers **P2**−**P4** was achieved using 10 mol % feed stock of the chromophore bisphenol and the remaining stoichiometric balance being 2,2-bis(4-hydroxyphenyl)hexafluoropropane (R = $C(CF_3)_2$). In all cases, the actual amount of chromophore segment incorporated into the polymers was confirmed by ^{19}F NMR analysis and was nearly the same as the calculated mol % feed stock (vide infra).

Polymers produced by this facile route are predominately enriched with 1,2-difluorovinylene (Z = CF═CF), formed via elimination of fluoride. Residual hydro-1,2,2-fluoroethane (Z = $CHFCF_2$) is also observed due to adventitious water or free phenol (Ar-OH).[20] The degree of unsaturation (Table 1) was determined by ^{19}F NMR spectroscopy on the basis of peak integrations. The quantitative conversion of monomer aryl TFVE to copolymer **P4** is easily confirmed by ^{19}F NMR spectroscopy (Figure 1). Aryl trifluorovinyl ether monomer 2 resonances are apparent from the diagnostic AMX pattern at −119.5 ppm (F_A), −126.4 ppm (F_M), and −133.8 ppm (F_X). The internal fluoroolefins in **P4** (Z = CF═CF) produce shifts at −120.8 and −122.0 ppm ((*Z*)-isomer) or −127.2 and −129.2 ppm ((*E*)-isomer). A (*Z*)/(*E*) ratio of about 1.2:1 is observed in all of the polymers investigated. Further utility of the polymerization strategy using catalytic carbonate bases such as Cs_2CO_3 enabled the preparation of analogous polymers (**P1′** and **P3′**) with primarily hydro-1,2,2-fluoroethane groups (Z = $CHFCF_2$) in place of fluoroolefin linkages. Also shown for **P4** in Figure 1, the -CF_2- formed an AB pattern at −85.7 and −86.2 ppm and the -CHF- produced broadened splitting at −141.2 ppm. This simple modification provides materials with similar thermal stability but with a more flexible backbone.

Selected physical properties for polymers **P1**−**P4** are provided in Table 1. The operationally simple polymerization procedure gave good yields (52−87%) of polymers. They are soluble in common organic solvents (THF, DMSO, and cyclopentanone) and produce optically transparent, free-standing films when spin- or drop-cast (see Figure 2c). Gel permeation chromatography (GPC) revealed number-average molecular weights (M_n) of 10300−36100 with agreeable polydispersities (M_w/M_n) of 1.5−2.8 expected from step-growth polymerization. DSC data indicate that the polymer systems are entirely amorphous with glass transition temperatures (T_g) ranging from 64−155 °C.

The semifluorinated FAVE polymers possess excellent thermal stability; thermal gravimetric analysis (TGA) shows average onset of decomposition temperature (T_d) of 353 and 360 °C in N_2 and air, respectively. Compared with well-studied CP systems, these polymers demonstrate similar stability in N_2 and higher stability in air, in many cases. Some notable examples for comparison include poly(phenylenevinylene) (PPV, T_d = 549 °C in N_2),[21a] poly[2-(3′,7′-dimethyloctyloxy)-5-methoxy-1,4-phenylenevinylene] (OC_1C_{10}-PPV, T_d = 426 °C in N_2),[21a] poly[2-methoxy-5-(2-ethylhexyloxy)]-1,4-phenylenevinylene (MEH-PPV, T_d = 360 °C in N_2 and 280 °C in air),[21b] poly(thiophene) (PT, T_d = 200−250 °C in air),[21c] and poly(pyrrole) (PP, T_d = 200−300 °C in N_2).[21d] To limit degradation of commercial CPs for PLED applications, they are encapsulated under vacuum to prevent exposure to air and moisture.[22] Furthermore, CPs are also subject to thermal fatigue and thermochromic effects that can compromise the photochemical properties of devices in which CPs are employed.[21a] Therefore, thermal stability in air is of major importance for device efficiency and operation lifetime, particularly for solar cells.[23]

Optical Properties. The physical properties of polymer fibers of **P1**−**P3** are shown in Figure 2 and reveal significant contrasts in color, white (**P1**) to yellow (**P2**) to green (**P3**), with a low loading of the respective chromophore (ca. 10 mol %). Furthermore, a 5 wt % polymer solution in THF, precipitated fiber, and a solvent cast film of **P2** revealed a high degree of luminescence upon exposure to a UV lamp (350 nm). Some key optical properties of **P1**−**P4** in solution (THF) and thin films are provided in Table 2. In all cases, emission spectra are recorded at excitation at λ_{max} from excitation spectra (Figures 3 and 4). A single $\pi-\pi^*$ absorption characteristic of fluorene and biphenyl functionalities is observed for **P1** (λ_{max} = 260 nm) in THF. Copolymers **P2**−**P4** produced two absorption bands in solution. The absorption band due to the $\pi-\pi^*$ transition of biphenyl moieties is present between 260−265 nm in all of the polymers, accompanied by bands attributable to the $\pi-\pi^*$ transition of the chromophore units spanning the range 350−450 nm (λ_R, Table 2). Absorption and emission maxima exhibited progressive red-shifting from **P1** through **P4**, as anticipated on the basis of the chromophore segments incorporated.

P1−**P4** films showed emission broadening compared with solutions and were more pronounced with the fluorene (**P1** series) and phenylenevinylene (**P2** series) polymers (Figure 4). Emission spectra for **P1** and **P1′** films displayed an approximately 19 nm red shift in λ_{em} to 560 nm, in addition to broadening of emission onset to near 600 nm. An even larger red shift of 38 nm was noted in the emission of **P2** films (620 nm), and broadening leads to emission onset near 650 nm. Films of **P3** series produced nominal red shifts compared with solution emission. The **P3** polymer series of films showed some emission broadening at the onset energy of about 650 nm retaining spectral features observed in solution emission. Within the **P1** (Figure 4a) and **P3** (Figure 4c) series, a larger percentage of polymers with rigid 1,2-difluorovinylene groups (where Z = CF═CF) led to greater emission band broadening in thin films versus their more flexible analogues (where Z = $CHFCF_2$). The inflexible nature of polymers enriched with 1,2-difluorovinylene groups are more pronounced in these films, while rigidity does not noticeably impact emission in dilute solution where emission derives from essentially independent chromophores (Figure 5). Out of the polymers studied, the solution and film emission

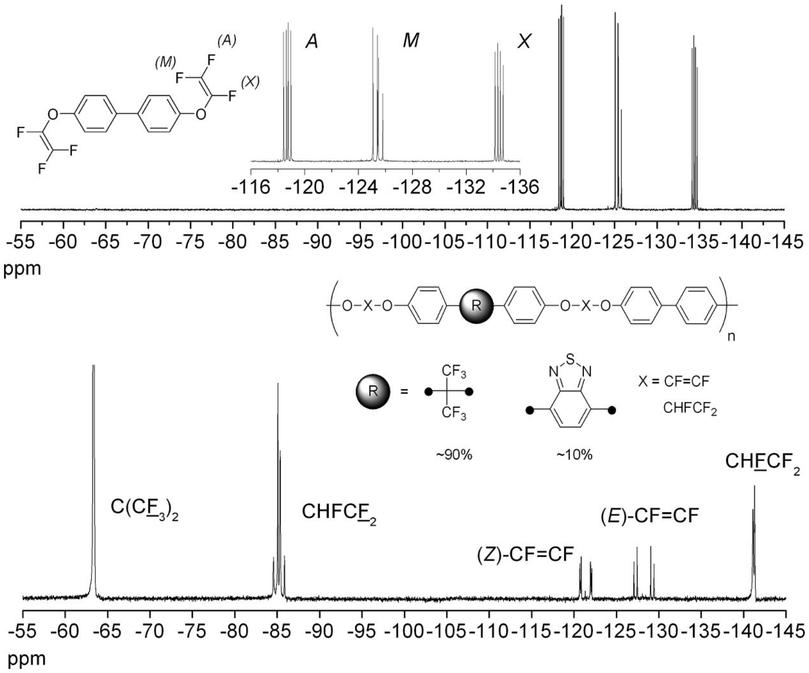

Figure 1. ^{19}F NMR (283 MHz) in DMSO-d_6 of monomer **2** (top) and copolymer **P4** containing 6F bisphenol A (bottom).

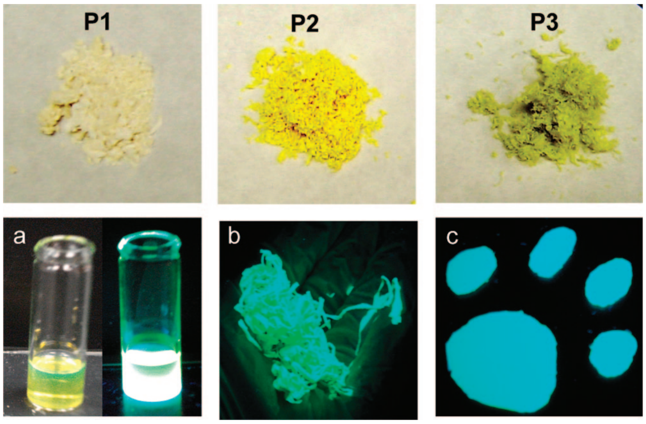

Figure 2. Pictures of chromophore-enriched, polymers **P1**−**P3** (top) and polymer **P2** (bottom) in (a) THF solution (ca. 5 wt % solids) in visible light (left) and under a UV lamp (right, 350 nm), (b) as a precipitated fibrous polymer under UV lamp (350 nm), and (c) free-standing film by solvent casting in a prefabricated template (Clemson tiger paw).

Table 2. Optical Properties of Polymers P1−P4

entry	abs λ_R (nm)[a] soln$_{THF}$ (film)	PL λ_{max} (nm) soln$_{THF}$ (film)	% Z = CF=CF[b]	Φ_F soln$_{THF}$
P1	260 (270)	310 (329)	80	0.09[c]
P1′	260 (260)	311 (328)	22	0.12[c]
P2	393 (393)	443 (481)	73	0.10[d]
P3	376 (376)	457 (459)	83	0.24[d]
P3′	376 (372)	453 (459)	53	0.15[d]
P3″	376 (378)	455 (458)	7	0.18[d]
P4	380 (384)	492 (492)	70	0.56[d]

[a] λ_R refers to the absorption maximum for the π−π* transition attributed to chromophore units R shown at the bottom of Scheme 1. [b] Determined by ^{19}F NMR peak integration; about 1.2:1 (*Z*)/(*E*) isomers. [c] Referenced to D-tryptophan in deionized water at pH 7.2 ($\Phi_F = 0.14$).[24] [d] Referenced to quinine sulfate in 0.1 M H_2SO_4 ($\Phi_F = 0.546$).[25]

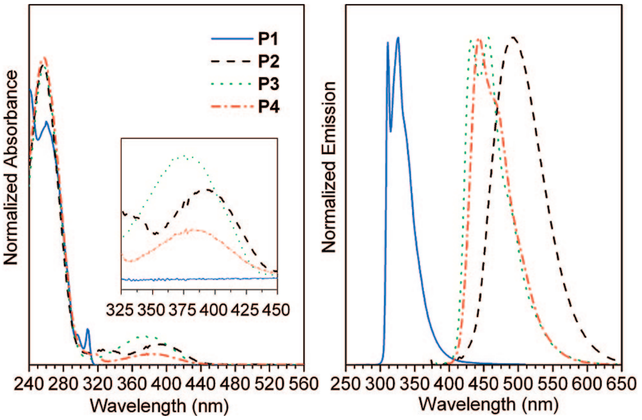

Figure 3. Absorption (left) and emission (right) spectra of polymers **P1**−**P4** in THF solution (ca. 1 mg/mL).

bands of **P4** showed strikingly similar features, suggesting that, even in the solid state, the thiadiazole chromophore units are effectively shrouded from each other by the fluoropolymer matrix.

Overall, polymers **P1**−**P4** produced large Stokes shifts of 50−112 and 59−108 nm in solutions and as thin films, respectively. This similarity in solution and thin films suggests the aryl ether polymer matrix that shrouds the excited chromophore segments, thus eliminating effective inter- or intrachain communication.[26] Polymers **P1**, **P3**, and **P4** produced nearly the same Stokes shifts in solution and film, whereas **P2** gave a Stokes shift of 50 nm in solution and 88 nm as a thin film.

Chain flexibility also impacts the fluorescence quantum yield (Φ_F) of FAVE polymers. Rigid materials tend to produce higher Φ_F values in π-conjugated polymers as compared to more flexible systems; this phenomenon has been attributed to attenuation of vibrational contributions to nonradiative decay pathways.[26] However, comparison of solution Φ_F values of Z-segment substitution within polymer series **P1** and **P3** were similar, indicating that these materials are not subject to the same type of interference as π-conjugated emissive materials. Overall, solution Φ_F values ranged from 0.09−0.56 for **P1**−**P4**, the highest value observed for the thiadiazole incorporated polymer (**P4**).

Conclusions

We have prepared a new class of solution processable semiconjugated fluorinated arylene vinylene ether (FAVE)

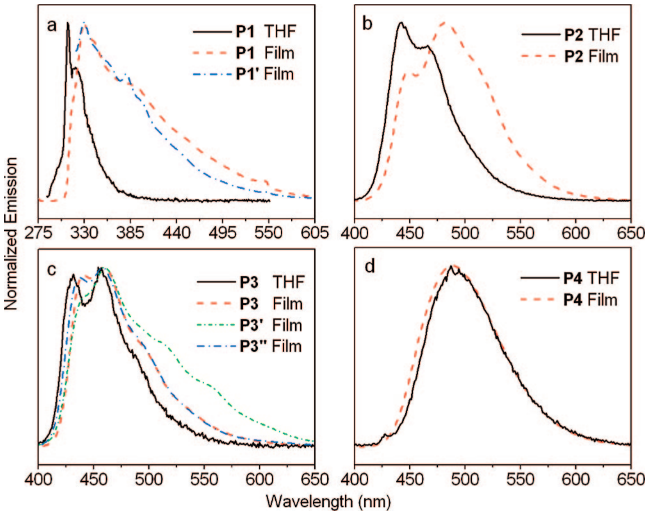

Figure 4. Comparison of normalized emission spectra of polymer series: (a) **P1**; (b) **P2**; (c) **P3**; and (d) **P4** in THF solution (ca. 1 mg/mL) and thin film (ca. 150−200 nm thick).

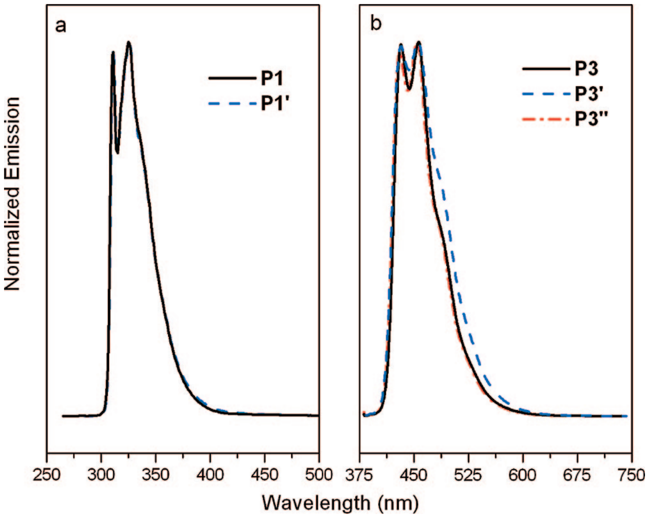

Figure 5. THF solution (ca. 1 mg/mL) emission of polymer series (a) **P1** and (b) **P3**.

polymers that can be modularly enriched with chromophore segments affording tunable photoluminescence in solution and solid state. The ability to modularly install chromophores would lead to the possibility of preparing mixed chromophore systems producing materials capable of hole or electron transport and white light emission. Because these polymers possess excellent solubility in organic solvent, these materials would compliment current casting techniques for device fabrication. Furthermore, we anticipate these materials would improve thermal stability thereby increasing the lifetime of a device. Preliminary studies have also been undertaken to extend the utility of these polymers to optical sensing. These studies reveal that **P3** and a metallated bipyridyl-modified FAVE polymer exhibited a highly selective emission enhancement in response to fluoride and cyanide ion. Details of these studies are described elsewhere.[27]

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