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Mixed Chromophore Perfluorocyclobutyl (PFCB) Copolymers for Tailored Light Emission

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ABSTRACT: Versatile intermediates 4-bromo(trifluorovinyloxy)benzene or 4-trifluorovinyloxyphenylboronic acid pinacol ester undergo a one step Suzuki coupling reaction with commercial aryl diboronic acids or aryl dibromides and afforded three new aryltrifluorovinylether chromophore monomers. The structures of these monomers were confirmed by ^{1}H, ^{19}F, and ^{13}C NMR spectroscopy and elemental (C, H, and N) combustion analysis. The monomers were readily polymerized via thermal [2 + 2] cyclopolymerization to form chromophore containing PFCB polymers with high molecular weights (Mn = 16 700−22 000), superb thermal stability T_d > 450 °C, and excellent processability. Photoluminescence studies reveal that the fluorinated ether linkage has no effect on lumiphore emission wavelength or solution quantum yields. Copolymerization affords a facile route to tailored emission from a linear polymeric system that includes a broad range of the visible spectrum. The properties of these polymers were analyzed by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), gel permeation chromatography (GPC), and absorbance and photoluminescence spectroscopy.

Introduction

The discovery of efficient electroluminescent (EL) organic conjugated polymer thin films has generated a tremendous research effort toward the design and fabrication of organic or polymer light-emitting diodes (PLED).[1−3] Polymeric-based emissive displays have the potential to produce high contrast images while mitigating the cost, space, weight, and high power consumption of inorganic based devices. Single color PLEDs based on polyphenylenevinylene (PPV) and polyfluorene are well established and used in a limited number of commercial products. However, recently, the potential to tune the emission of a single polymer has focused a great deal of research toward the construction of devices which appear white to the human eye.[4,5] A single polymer which emits over a broad spectral range has a number of advantages over a polymer blend or a blend of small molecules. Polymer and small molecule chromophore blends have been shown to produce white light.[3] However, they typically translate to poor devices that are prone to failure due to phase separation, and they tend to be more difficult to process than a polymer system.[6] More recently, the covalent introduction of a variety of fluorescent and phosphorescent dyes to polyfluorene has created linear polymers with white or very near white emission with relatively efficient electroluminence.[7] While the covalent attachment of dyes to polyfluorene produces white emission, the multistep monomer synthesis can be arduous and costly. Furthermore, it is difficult to remove the residual Pd from Suzuki type polymerizations which has detrimental effects on device performance.[8]

Here we report the synthesis of a modular chromophore polymer based on the cyclodimerization of aryltrifluorovinyl ethers to form perfluorocyclobutyl (PFCB) polymers. PFCB polymers have enjoyed a great deal of interest as passive optical materials due to their high T_g, high thermal stability, superior optical clarity into the near IR, and broadly tailorable compositions.[9−12] These properties also make them good candidates for materials in active optics such as PLED's. The use of fluorinated polymers has been shown to decrease aggregation and prevent eximer formation resulting in increased EL brightness at reduced turn on voltages.[13] The ability to functionalize a very wide variety of substrates with trifluorovinyl ethers (TFVE) allows for the construction of copolymers with nearly any composition desired.[9−12] For example, PFCB based charge transport materials have also shown promise in increasing the efficiency of PLED's.[14−16] Here we report the synthesis, characterization, and polymerization of three TFVE chromophore monomers. Photoluminescence studies show that the emission of the materials can be tuned by varying the monomer ratio.

Experimental Section

Materials. 4-Bromo(trifluorovinyloxy)benzene, 4-trifluorovinyloxyphenylboronic acid pinacol ester, bis(trifluorovinyloxy)biphenyl (**M4**), and 1,1,1-triphenyltrifluorovinyloxyethane (**M5**) starting materials were generously donated by Tetramer Technologies, LLC (Pendelton, SC), and are available commercially through Oakwood Products, Inc. (oakwoodchemical.com, Columbia, SC). Tetrakis(triphenylphosphine)palladium(0) was purchased from Strem and THF solvent was purified on a Pure Solv 400−2-D solvent purification system. All other reagents where purchased from Aldrich and used without further purification.

Instrumentation. All ^{1}H, ^{13}C, and ^{19}F NMR spectra were obtained using either a JEOL Eclipse 300 spectrometer collected in $CDCl_3$ with TMS as the standard. Absorption spectroscopy was performed on a Perkin-Elmer Lamba 900 spectrophotometer, and photoluminescence spectroscopy was performed on a Horiba Jobin Yvon Fluorolog 3-222Tau photoluminescence spectrometer. Gel permeation chromatography (GPC) data was obtained using a Waters 2690 in $CHCl_3$ and polystyrene standards. Thermal gravi-

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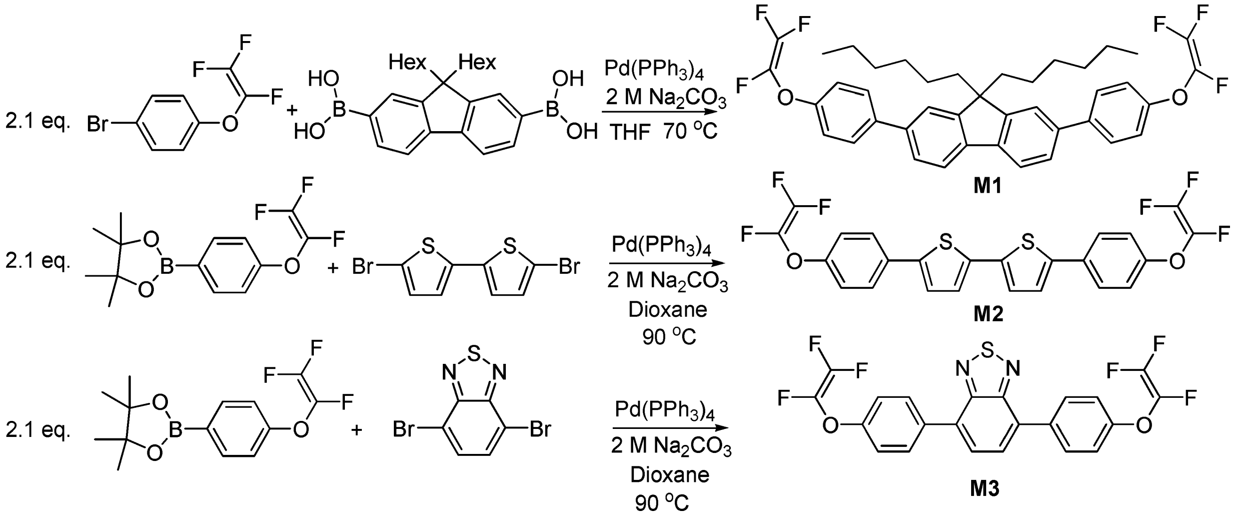
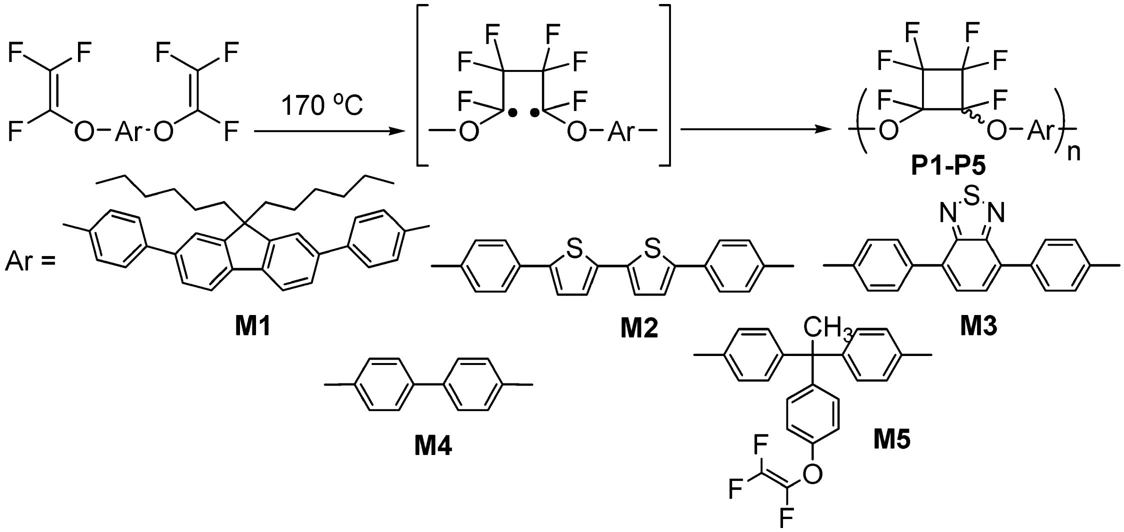
Scheme 1. Synthesis of Trifluorovinyl Ether Chromophore Monomers.



Scheme 2. Polymerization of Trifluorovinyl Ether Monomers.



metric analysis (TGA) data was obtained from a Mettler-Toledo 851 TGA/SDTA System at a heating rate of 5 °C min^{-1} in a nitrogen atmosphere. Differential scanning calorimetry (DSC) was obtained from a TA Instruments Q1000 system with an auto sampler and liquid nitrogen cooling system. Analysis was carried out using TA Instruments Universal Analysis software. The glass transition temperature (T_g) was obtained from a second reheating curve after cooling at 10 °C /min. The reported T_g value was taken at the midpoint of the C_p curve. Monomer melting points were determined via DSC at a heating rate of 5 °C /min. Combustion analysis was performed on a Perkin-Elmer Series II 2400 CHNS/O analyzer and an average of three runs for each sample is reported.

Synthesis of 9,9-Dihexyl-2,7-phenyltrifluorovinyloxyfluorene (M1). 9,9-Dihexylfluorene-2,7-diboronic acid (922 mg, 2.18 mmol), 4-bromo(trifluorovinyloxy)benzene (1.16 g, 4.59 mmol), 2 M (aq) Na_2CO_3 (8 mL), and anhydrous THF (30 mL) were added to a 50 mL two-neck round-bottom flask equipped with a N_2 inlet, magnetic stirbar, and a reflux condenser. The reaction mixture was allowed to stir until all reagents had fully dissolved; the solution was then sparged with N_2 for 10 min. Next, $Pd(PPh_3)_4$ (250 mg, 0.22 mmol) was added, and the reaction mixture was refluxed at 70 °C for 24 h. The reaction mixture was poured into H_2O (50 mL) and extracted with CH_2Cl_2 (3 × 25 mL). The organic layer was separated, dried ($MgSO_4$), filtered, and concentrated under vacuum. The solid was then recrystallized from MeOH and filtered over alumina (THF) to yield 9,9-dihexyl-2,7-phenyltrifluorovinyloxyfluorene (**M1**) as a white solid in a 70% yield (1.03 g). Mp (DSC): 102 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.78 (d, $J = 7.9$ Hz, 1H), 7.67 (d, $J = 8.2$ Hz, 2H) 7.55 (d, $J = 7.9$ Hz, 1H), 7.51 (s, 1H), 7.23 (d, $J = 8.6$ Hz, 2H), 2.06 (t, $J = 6.6$ Hz, 2H), 1.14−1.07 (m, 8H), 0.77 (t, $J = 3.42$, 3H). ^{19}F NMR (282 MHz, $CDCl_3$, δ): −133.4 (dd, $J = 59.2$, 111.9 Hz, 1F), −126.0 (dd, $J = 98.7$, 111.9 Hz, 1F), −119.2 (dd, $J = 59.2$, 95.4 Hz, 1F). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 14.07, 22.65, 23.89, 29.77, 31.54, 40.50, 55.40, 116.31, 120.22, 121.46, 126.05, 128.79, 138.7, 139.05, 140.15, 151.86. Anal. Calcd for $C_{41}H_{40}F_6O_2$: C, 72.55; H, 5.94; F, 16.79; O, 4.71. Found: C, 72.41; H, 5.70.

Synthesis of 5,5-Phenyltrifluorovinyloxybisthiophene (M2). 4-Trifluorovinyloxyphenylboronic acid pinacol ester (1.02 g, 3.39 mmol), 5,5-dibromobisthiophene (0.5 g, 1.54 mmol), 2 M (aq) Na_2CO_3 (4 mL), and anhydrous dioxane (10 mL) were added to a 50 mL two-neck round round-bottom flask equipped with a N_2 inlet and a reflux condenser. The reaction mixture was allowed to stir until all reagents had fully dissolved; the solution was then sparged with N_2 for 10 min. Next $Pd(PPh_3)_4$ (200 mg, 0.17 mmol) was added and the reaction mixture was heated at 100 °C for 24 h. The reaction mixture was poured into H_2O (40 mL) and extracted with EtOAc (3 × 25 mL). The organic layer was separated, dried ($MgSO_4$), filtered, and concentrated under vacuum. The solid was washed repeatedly with MeOH to remove the monosubstituted product and filtered over alumina (THF) to yield 5,5-phenyltrifluorovinyloxybisthiophene (**M2**) as a bright yellow solid in a 40% yield (0.31 g). Mp (DSC): 77 °C. ^{1}H NMR (300 MHz, DMSO-d_6, δ): 7.74 (d, $J = 8.6$ Hz, 4H), 7.50 (d, $J = 3.8$ Hz, 2H) 7.36 (d, $J = 3.8$ Hz, 2H), 7.35 (d, $J = 8.9$ Hz, 1H). ^{19}F NMR (282 MHz, DMSO-d_6, δ): −134.1 (dd, $J = 59.4$, 107.9 Hz, 1F), −125.6 (dd, $J = 97.9$,

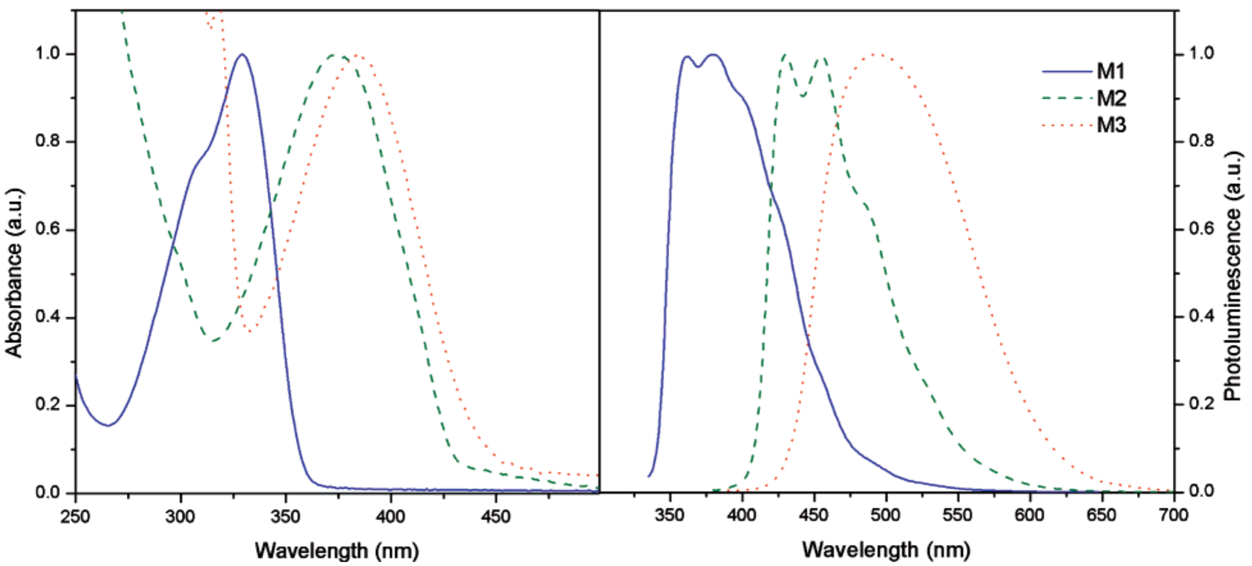


Figure 1. Absorbance and photoluminescence (λ_{max} excitation) spectra of TFVE chromophore monomers as a dilute solution in THF. The emission of the chromophores cover a 120 nm span and the absorption and emission values are consistent with the literature values for the model compounds without the TFVE groups.[18−20]

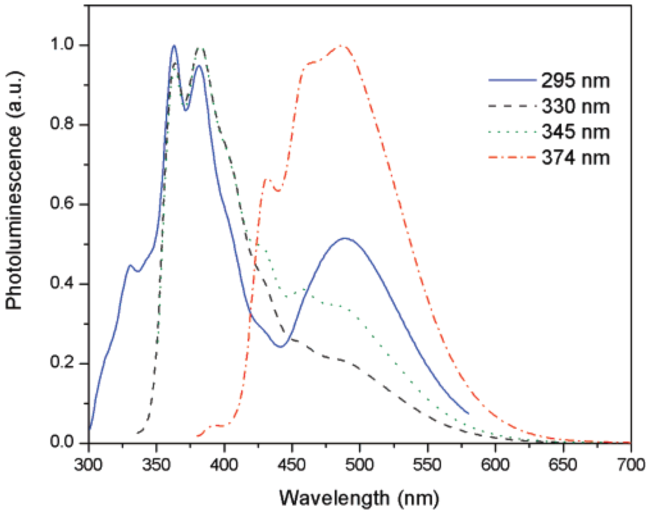


Figure 2. Photoluminescence overlay of the terchromophoric polymer (**P4**) at various excitation wavelengths in a dilute THF solution. The emission of the material is dependent upon the excitiation wavelength. Emission is dominated by the chromophore that corresponds to the excitation wavelength ($\lambda_{exc} = 330$ nm produces a blue emission from the fluorene, $\lambda_{exc} = 374$ nm produces a green emission from the thiophene and benzothiadiazole). When the material is excited at the wavelength of the host monomer **M4** ($\lambda_{exc} = 295$ nm) energy transfer excites all chromophores producing a very broad emission.

112.4 Hz, 1F), −117.6 (dd, $J = 59.3$, 95.7 Hz, 1F). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 123.83, 124.57, 125.93, 128.12, 129.86, 136.32, 137.69, 147.63. Anal. Calcd for $C_{24}H_{12}F_6O_2S_2$: C, 56.47; H, 2.37; F, 22.33; O, 6.27; S, 12.56. Found: C, 56.04; H, 2.18.

Synthesis of 4,7-Phenyltrifluorovinyloxybenzothiadiazole (M3). 4-Trifluorovinyloxyphenylboronic acid pinacol ester (1.0 g, 3.3 mmol), 4,7-dibromo-2,1,3-benzothidiazole (0.445 g (1.5 mmol), 2 M (aq.) Na_2CO_3 (4 mL), and anhydrous dioxane (10 mL) were added to a 50 mL two neck round round-bottom flask equipped with a N_2 inlet and a reflux condenser. The reaction mixture was allowed to stir until all reagents had fully dissolved; the solution was then sparged with N_2 for 10 min. Next $Pd(PPh_3)_4$ (200 mg, 0.17 mmol) was added, and the reaction mixture was heated at 90 °C for 24 h. The reaction mixture was poured into H_2O (50 mL) and extracted with EtOAc (3 × 25 mL). The organic layer was separated, dried ($MgSO_4$), filtered, and concentrated under vacuum. The solid was then recrystallized with MeOH and filtered over alumina (THF) to yield 4,7-phenyltrifluorovinyloxybenzothiadiazole (**M3**) as a bright green solid in a 61% yield (0.439 g). Mp (DSC): 153 °C. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 7.97 (d, $J = 8.6$ Hz, 4H), 7.74 (s, 2H), 7.28 (d, $J = 8.6$ Hz, 4H). ^{19}F NMR (282 MHz, CDCl$_3$, δ): −133.5 (dd, $J = 59.2$, 108.6 Hz, 1F), −125.7 (dd, $J = 98.7$, 113.0 Hz, 1F), −119.0 (dd, $J = 59.2$, 95.5 Hz, 1F). ^{13}C NMR (75 MHz, DMSO-d_6, δ): 113.9, 114.12, 139.83, 140.21, 142.47, 148.56. Anal. Calcd for $C_{22}H_{10}F_6N_2O_2S$: C, 55.01; H, 2.10; F, 23.73; N, 5.41; O, 6.66; S, 6.68. Found: C, 55.92; H, 2.37; N, 5.19.

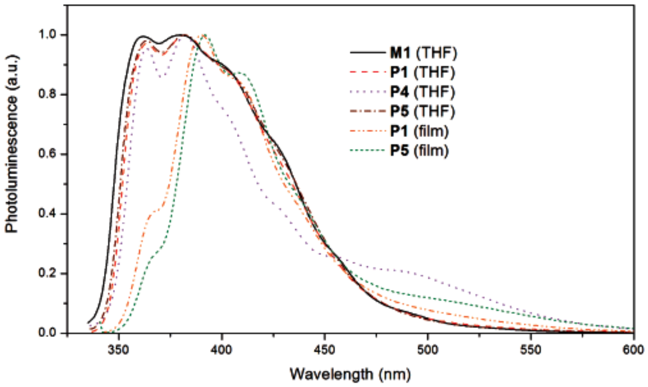


Figure 3. Photoluminescence overlay of all materials containing **M1** at $\lambda_{exc} = 330$ nm. The emission is independent of the fluorinated group.

Synthesis of P1. Bistrifluorovinyloxybiphenyl monomer (**M4**) (500 mg, 1.4 mmol) and 9,9-dihexyl-2,7-phenyltrifluorovinyloxyfluorene (**M1**) (50 mg, 0.07 mmol) were added to a flame-dried glass ampule. The reaction mixture was heated to melting under a high vacuum to remove any remaining solvent, and then sealed. The ampule was placed in a sand bath at 180 °C for 24 h, then allowed to return to room temperature and opened. The solid polymer was dissolved in a minimum amount of THF, precipitated into a large excess of MeOH, filtered, and washed repeatedly with MeOH to yield **P1** (496 mg) as a fibrous white solid in 90% isolated yield. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 7.46 (d, $J = 7.3$ Hz, 1H), 7.21−7.13 (m, 1H). ^{19}F NMR (282 MHz, CDCl$_3$, δ): −127.41, −127.53, −128.26, −128.49, −129.22, −129.89, −130.05, −130.67, −130.97, −131.28.

Synthesis of P2. Biphenyltrifluorovinyl ether monomer (**M4**) (500 mg, 1.4 mmol) and 5,5-phenyltrifluorovinyloxybisthiophene

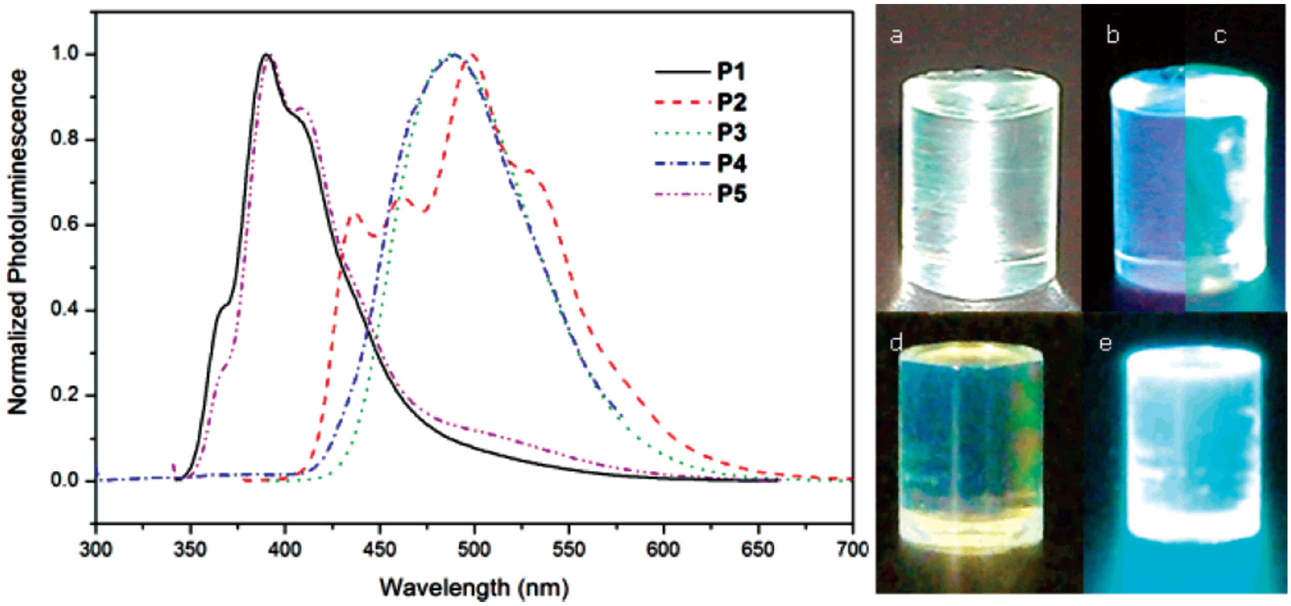


Figure 4. Solid-state PL overlay (λ_{max} excitation) of copolymers **P1**−**P5** as thin films (left) and photographs of mixed chromophore PFCB networks (right) (1 cm diameter) at 0.15 wt % total chromophore under ambient light (a), 254 nm light (b), and 365 nm light (c) and 7.5 wt % total chromophore under ambient light (d), and 365 nm light (e).

(**M2**) (50 mg, 0.098 mmol) were polymerized following the procedure for the preparation of **P1** to yield **P2** (476 mg) as a bright yellow fibrous solid in 87% isolated yield. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 7.47 (d, $J = 7.9$ Hz, 1H), 7.23−7.15 (m, 1H). ^{19}F NMR (282 MHz, CDCl$_3$, δ): −127.75, −127.89, −128.00, −128.54, −128.68, −129.39, −130.07, −130.18, −130.86, −130.96, −131.22.

Synthesis of P3. Biphenyltrifluorovinyl ether monomer (**M4**) (500 mg, 1.4 mmol) and 4,7-phenyltrifluorovinyloxybenzothiadiazole (**M3**) (50 mg, 1.04 mmol) were polymerized following the procedure for the preparation of **P1** to yield **P3** (489 mg) as a light green fibrous solid in 89% isolated yield. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 7.45 (d, $J = 7.2$ Hz, 1H), 7.21−7.13 (m, 1H). ^{19}F NMR (282 MHz, CDCl$_3$, δ): −126.63, −127.81, −127.93, −128.60, −128.72, −129.24, −129.43, −130.12, −130.22, −130.91, −130.99, −131.25.

Synthesis of P4. Biphenyltrifluorovinyl ether monomer (**M4**) (500 mg, 1.4 mmol), 9-dihexyl-2,7-phenyltrifluorovinyloxyfluorene (**M1**) (50 mg, 0.07 mmol), 5,5-phenyltrifluorovinyloxybisthiophene (**M2**) (50 mg, 0.098 mmol), and 4,7-phenyltrifluorovinyloxybenzothiadiazole (**M3**) (50 mg, 1.04 mmol) were polymerized following the procedure for the preparation of **P1** to yield **P4** (523 mg) as a light green fibrous solid in 80% isolated yield. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 7.45 (d, $J = 7.2$ Hz, 1H), 7.21−7.13 (m, 1H). ^{19}F NMR (282 MHz, CDCl$_3$, δ): −126.44, −127.65, −127.87, −128.46, −128.69, −129.24, −129.52, −130.07, −130.25, −130.87, −131.03, −131.28.

Synthesis of P5. 9-Dihexyl-2,7-phenyltrifluorovinyloxyfluorene (**M1**) (300 mg, 0.07 mmol) was polymerized following the procedure for the preparation of **P1** to yield **P5** (256 mg) as a beige fluffy solid in 85% isolated yield. ^{1}H NMR (300 MHz, CDCl$_3$, δ): 7.75−7.73 (m, 1H), 7.67−7.63 (m, 2H) 7.54−7.52 (m, 2H), 7.34−7.25 (m, 2H), 2.02 (m, 2H), 1.10−1.04 (m, 8H), 0.77 (t, $J = 6.19$, 3H). ^{19}F NMR (282 MHz, CDCl$_3$, δ): −127.46, −127.76, −128.26, −128.55, −129.26, −129.91, −130.06, −130.70−130.88, −131.27.

Preparation of PFCB Chromophore Networks. 1,1,1-Triphenyltrifluorovinyloxyethane (**M5**) (2 g, 3.66 mmol), phenyltrifluorovinyloxyfluorene (**M1**) (1 mg, 0.0015 mmol), 5,5-phenyltrifluorovinyloxybisthiophene (**M2**) (1 mg, 0.002 mmol), 4,7-phenyltrifluorovinyloxybenzothiadiazole (**M3**) (1 mg, 0.002 mmol) were added to a flame-dried glass ampule. The reaction mixture was heated past its melting point under a high vacuum to remove any remaining solvent and was then sealed. The ampule was placed in a sand bath at 180 °C for 24 h. The ampule was allowed to return to room temperature and opened to yield a clear, 0.15% chromophore containing PFCB cross-linked glass in the shape of the ampule. The same procedure was used to make the 7.5% glass using the following stoichiometry: 1,1,1-triphenyltrifluorovinyloxyethane (2 g, 3.66 mmol), phenyltrifluorovinyloxyfluorene (**M1**) (50 mg, 0.074 mmol), 5,5-phenyltrifluorovinyloxybisthiophene (**M2**) (50 mg, 0.098 mmol), and 4,7-phenyltrifluorovinyloxybenzothiadiazole (**M3**) (50 mg, 0.104 mmol).

Results and Discussion

Monomer Synthesis. Monomers **M1**, **M2**, and **M3** were synthesized in one step from commercial products under Pd-catalyzed Suzuki conditions (Scheme 1). The yields for **M1** and **M3** were good, while the yield for **M2** suffered slightly due to poor solubility of the disubstituted product. Carrying out Suzuki chemistry in the presence of aryl-TFVE's provided some difficulty at first. The reactions were first attempted in DMF (a common Pd coupling solvent) and failed due to the polar solvent facilitating Pd coordination and thus undesired addition chemistry to the TFVE. DME also proved unsuccessful due to problems with product solubility. Dioxane proved to be the solvent of choice for **M2** and **M3**, and THF was the best for the synthesis of **M1**. Monomer purification was accomplished via recrystallization from MeOH followed by filtration over alumina to remove any residual Pd catalyst. All three monomers structures were confirmed by ^{19}F, ^{1}H, and ^{13}C NMR spectroscopy, and elemental (C, H, and N) combustion analysis.

Polymerization. The homopolymerization of **M1**−**M3** was carried out in a sealed ampule under vacuum at 180 °C (Scheme 2). Unfortunately, only **M1** yielded a soluble homopolymer, most likely due to the solubilzing hexyl groups at the 9,9 position of the fluorene. Polymerization of monomers **M2** and **M3** were observed by DSC, however NMR and molecular weight characterization was not possible due to insolubility. The loss of solubility in homopolymers from **M2** and **M3** is not surprising due to their rigid and polar aromatic structure. Similar insolubility was observed for previously reported oligophenylene PFCB polymers.[17] In order to produce soluble polymer, **M1**−**M3** were copolymerized (10 wt % chromophore) with commercially available biphenyl monomer (**M4**). Copolymerization produced soluble copolymers with good molecular weight. These materials are readily soluble in common organic solvents,

Table 1. Selected Properties of Monomers M1−M3

monomer	T_m/°C[a]	λ_{max}/nm[b]	ems/nm[c]	Φ[d]
M1	102	331	363, 380	0.43
M2	77	374	430, 456	0.18
M3	153	385	493	0.61

[a] DSC (5 °C min^{-1}) in nitrogen, first heating. [b] Solution absorption in THF. [c] Solution emission in THF at λ_{max}. [d] Quantum yield measured using quinine sulfate as a standard.[21]

film forming, and can be processed in a similar fashion to typical PFCB materials.[9,10] The copolymers showed remarkable thermal stability with decomposition temperatures over 450 °C and T_g values around 150 °C (Table 2). In addition to single chromophore copolymers a copolymer with all three chromophores in a 5% by weight ratio was synthesized (**P4**). This polymer was also easily solution processed into films and exhibited the same thermal stability and high T_g of the other materials. Finally, two cross-linked glasses with **M5** were prepared with all three of the chromophores (0.15 wt % and 7.5 wt %, Figure 4).

Optical Characterization. The luminescent properties of these materials were studied by UV−vis absorption and photoluminescense spectroscopy in both solution and thin film. Fluorene-TFVE (**M1**) showed a maximum in absorption at 330 nm and a maximum in photoluminescence at 380 nm. Bisthiophene−TFVE (**M2**) and benzothiadiazole−TFVE (**M3**) were both green emitters with absorption maxima at 374 and 384 nm and photoluminescence maxima at 430 and 493 nm, respectively. The absorption and emission values for **M1**−**M3** match almost identically the literature values for the model compounds without the TFVE groups.[18−20] The shape of the emission curves also matches well to the literature with **M1** and **M2** showing characteristic multiple emission bands. Thus, the TFVE group is a means of polymerizing chromophores without effecting chromophore emission. Solution-phase photoluminescent quantum efficiencies were calculated for the monomers.[21,22] All monomers showed high quantum yields, but the benzothidiazole was by far the most efficient at 61%. **M1** and **M2** exhibited quantum efficiencies of 44% and 18%, respectively. The calculated quantum yields for these materials are consistent with the literature values for the model compounds. Solution state quantum yields were also calculated for the 10% chromophore/**M4** copolymers (**P1**−**P3**). All chromophores exhibited similar efficiency when copolymerized with **M4**, with **M3** again showing the highest efficiency at 58% for the copolymer. It was encouraging to observe that chromophore emission remains the same for the monomers and their resulting polymers in solution.

One of the major advantaged of TFVE polymerizations is the modular ability to copolymerize many monomers into a random copolymer with tailored properties. In particular, the photophysical properties of mixed chromophore copolymer (**P4**) were studied. The solution state PL (Figure 2) shows the emission from all three chromophores yet the overall emission of the material is dependent upon the excitation wavelength. When the copolymer is excited at the wavelength for one chromophore, the copolymer emission was dominated by that chromophore. Even more exciting is when terchromophore polymer **P4** is excited at the absorption wavelength for **M4**, the biphenyl unit appears to facilitate energy transfer evenly, thus providing a very broad emission approaching white light. Further evidence that the presence of the PFCB ring has no significant optical effect on chromophore emission is shown in Figure 3.

Spun cast films for the **M1** and **M3** polymer systems gave similar results to the solution data. However, the thiophene based copolymer (**P2**) showed significant red shifting, most likely due to aggregation of the highly aromatic system **M2**. Unlike the solution data, solid-state PL studies revealed that the **P4** system readily underwent energy transfer to the benzothiadiazole chromophore (**M3**) thus resulting in only green emission. Previous white light emitting poly(fluorene)-based materials discussed earlier rely on such energy transfer to produce the desired emission.[6] The effect of energy transfer on the emission of the materials is demonstrated in Figure 4. Mixed chromophore PFCB network glasses were prepared using a trifunctional monomer (**M5**)[9] in place of **M4**. When the concentration of the chromophore monomers is low, the emission is dependent upon the excitation wavelength similar to **P4** in solution. Increasing the chromophore concentration facilitates energy transfer to the lower energy benzothiadiazole (**M3**) moiety, and only green emission is observed regardless of excitation wavelength. Work is currently under way to tune the concentration of the chromophores in the polymers to obtain the desired emission in the solid state.

Conclusions

Perfluorocyclobutyl polymer chemistry provides an efficient modular platform for the copolymerization of multiple lumiphore system without affecting the emission. In addition the PFCB linkage provides an amorphous material, superb optical clarity, enhanced solubility, and high thermal stability. Three TFVE functionalized chromophores have been synthesized and characterized. These materials are easily prepared in one step from commercial precursors, and can be readily copolymerized into linear polymers. Photoluminescence studies show that TFVE and PFCB groups have little effect on the emission of the chromophore, showing that the PFCB linkage can act as an optically inert pathway for the construction of mixed chromophore emissive materials. Network glasses were prepared by copolymerization from neat monomer, to demonstrate how chromophore concentration affects emission. Work is currently under way to tune the emission of these materials into the red region by introducing a TFVE functionalized phosphorescent Ir[III] complex,[22] increase the charge carrying properties of these polymers by introducing TFVE functionalized oxadiazole and carbazole functionality,[23] and construct electroluminescent devices from these materials.

Table 2. Selected Polymer Properties

polymer	composition (feed ratio)[a]	T_g/°C[b]	T_d/°C[c]	$M_n \times 10^{-3}$ [d]	M_w/M_n	λ_{max}/nm[e]	ems/nm[f]	Φ[g]
P1	**M1:M4** (1:10)	138	487	22.3	2.52	258	362, 382	0.44
P2	**M2:M4** (1:10)	146	491	22.1	2.65	254	431, 456	0.23
P3	**M3:M4** (1:10)	158	453	19.1	3.57	255	491	0.58
P4	**M1:M2:M3:M4** (1:1:1:20)	140	467	18.2	2.68	256	363[h]	0.49
P5	**M1**	138	484	16.7	2.66	331	382	0.39

[a] Monomer composition and weight feed ratio. [b] DSC (10 °C min^{-1}) in nitrogen, second heating. [c] TGA onset at 5 °C min^{-1} in N_2. [d] GPC in $CHCl_3$ using polystyrene standards. [e] Solution absorption in THF. [f] Solution emission in THF at λ_{max}. [g] Quantum yield measured using quinine sulfate as a standard.[21] [h] Multiple emissions, see Figure 2.

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