

Synthesis and characterization of highly fluorescent phenylene vinylene containing perfluorocyclobutyl (PFCB) aromatic ether polymers

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ABSTRACT

4-(Trifluorovinyloxy)benzaldehyde was treated under Wittig conditions with 4-dihexyloxy-2,5-xylenebis(triphenylphosphoniumbromide) to form 1,4-bis(2'-(4-trifluorovinyloxyphenyl)ethenyl)-2,5-dihexyloxybenzene, a novel phenylene vinylene-bistrifluorovinyl ether monomer. Cyclopolymerization afforded an insoluble, non-luminescent material likely due to cross-addition reactions between phenylene vinylene olefin and trifluorovinyl ether (TFVE). However, 1,2-bis(4-formylphenoxy)hexafluorocyclobutane was polymerized with 1,4-dihexyloxy-2,5-xylenebis(triphenylphosphoniumbromide) and 1-methoxy-4-(2-ethylhexyloxy)-2,5-xylenebis(triphenylphosphoniumbromide) under Wittig conditions to yield two novel poly(perfluorocyclobutyl-co-phenylene vinylene) polymers. The polymers are of moderate molecular weight (8600–8700 M_n), show excellent thermal stability ($T_d = 390$ – 405 °C), and are readily soluble in common organic solvents. The materials are highly fluorescent in both solution and thin film with solution quantum yields of 68 and 71%.

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1. Introduction

Poly(*p*-phenylene vinylenes) (PPVs) are a synthetically diverse class of organic conjugated polymers that have stimulated research towards their use in a wide array of optics applications. In addition to being the first materials used in polymer electroluminescent devices [1], their potential applications include: field effect transistors [2], photovoltaic devices [3], electrochromics [4], and organic diode lasers [5,6]. PPV materials have received interest in these applications due to the ability to tune their luminescent and physical properties by altering side chains [7], via introducing kinks in the polymer backbone [8], and through variation in comonomer identity [9].

Perfluorocyclobutyl (PFCB) aromatic ether polymers are semi-fluorinated organic polymers with high performance properties such as high thermal and chemical stabilities, excellent optical clarity across the spectrum, and broad synthetic versatility [10]. These characteristics have led to interest in their use in high performance optics [11], polymer light emitting diode charge transport layers [12], quantum dot encapsulation [13], and organic nanomaterials [14]. PFCB polymers can be accessed via two synthetic pathways from aromatic trifluorovinylethers (TFVE) (Scheme 1). In

Path 1, difunctional TFVE monomers prepared from commercial phenolics [10] or the versatile bromo trifluorovinyl ether intermediate **1** [15] undergo a thermally activated [2 + 2] cyclopolymerization to form PFCB polymers. Alternatively, a monofunctional TFVE can be thermally cyclo-dimerized to form a PFCB dimer that can undergo polymerization via standard step growth chemistry (**Path 2**). Having two polymerization routes to PFCB polymers allows for the synthesis of a wide range of soluble yet robust PFCB containing materials.

Recently PFCB polymers have been used to produce polymers with tailorable emission via copolymerization of trifluorovinyl ether chromophores [16]. The PFCB ring proved to be optically inert with no effect on chromophore emission. This fact combined with the thermal stability, optical clarity, processability and broad synthetic versatility makes PFCB linked chromophore systems as good candidates for use in a wide variety of applications from polymer light emitting diodes to organic lasers. In this paper we discuss the synthesis and properties of two highly luminescent poly(perfluorocyclobutyl-co-phenylene vinylene) polymers (Table 1) and a phenylene vinylene TFVE monomer.

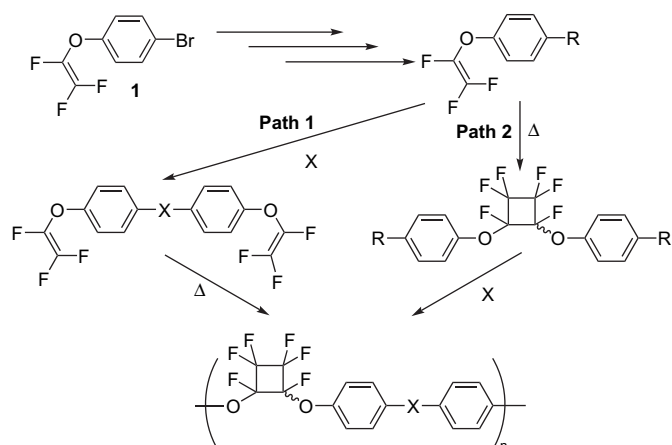
2. Experimental

2.1. Materials

All reagents were purchased and used without further purification unless otherwise noted. THF solvent was purified on a Pure

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Scheme 1. The two synthetic pathways to PFCB polymers from the versatile 4-bromo(trifluorovinyl)benzene **1** intermediate are demonstrated. **Path 1** involves the synthesis of a difunctional TFVE monomer followed by thermal cyclopolymerization. In **Path 2** TFVE cyclo-dimerization occurs prior to polymerization and the TFVE dimer is polymerized via standard step-growth polymerization chemistry.

Solv 400-2-D solvent purification system. 4-(Trifluorovinyl)oxybenzaldehyde and 1,2-bis(4-formylphenoxy)hexafluorocyclobutane were prepared from 4-(trifluorovinyl)oxy-bromobenzene as described previously [15]. 4-(Trifluorovinyl)oxybromobenzene and related PFCB intermediates, monomers, and polymers were generously donated by Tetramer Technologies, LLC (Pendleton, SC), and are available commercially through Oakwood Products, Inc. (oakwoodchemical.com, Columbia, SC). 1-Methoxy-4-(2-ethylhexyloxy)-2,5-xylenebis(triphenylphosphoniumbromide) (**5**) was prepared from 2,5-bis(bromomethyl)-1-methoxy-4-(2-ethylhexyloxy)benzene via Arbuzov rearrangement as described in the literature [17].

2.2. Instrumentation

^1H and ^{19}F NMR spectra were recorded on a JEOL Eclipse 300 spectrometer in CDCl_3 with TMS standard. Absorption and photoluminescence spectroscopy were performed on a Perkin Elmer Lambda 900 spectrophotometer and a Horiba Jobin Yvon Fluorolog 3-222Tau photoluminescence spectrometer, respectively. Gel permeation chromatography (GPC) data was obtained using a Waters 2690 in CHCl_3 by comparing with polystyrene standards. Thermal gravimetric analysis (TGA) data was obtained from a Mettler-Toledo 851 TGA/SDTA system at a heating rate of $10^\circ\text{C min}^{-1}$ in a nitrogen atmosphere. Differential scanning calorimetry (DSC) was performed on a TA instruments Q1000 system with an auto sampler and liquid nitrogen cooling system. Thermal analysis was carried out using TA Instruments Universal analysis software. Combustion analysis was performed on a Perkin Elmer Series II 2400 CHN analyzer and an average of three runs for each sample is reported.

Table 1

Properties of poly(perfluorocyclobutyl-co-phenylene vinylene) polymers

Polymer	$T_d/^\circ\text{C}^a$	$M_n \times 10^{-3}^b$	M_w/M_n	$\lambda_{\text{max}}^c/\text{nm}$ (THF)	Ems^d/nm (THF)	ϕ^e	$\lambda_{\text{max}}^f/\text{nm}$ (film)	Ems^g/nm (film)
PFCB-HO-PV	390	8.78	1.53	325, 392	445	0.68	336, 391	495
PFCB-MEH-PV	405	8.63	1.67	324, 379	442	0.71	330, 384	485

^a TGA onset at $10^\circ\text{C min}^{-1}$ in N_2 .

^b GPC in CHCl_3 using polystyrene standards.

^c Solution absorption in THF; bold number represents stronger band.

^d Solution emission in THF at λ_{max} .

^e Solution quantum yield measured using quinine sulfate as a standard.

^f Absorption of polymer thin film on quartz glass.

^g Thin film emission on quartz glass at λ_{max} .

2.3. Synthesis of 1,4-bis(2'-(4-trifluorovinyl)oxyphenyl)ethenyl)-2,5-dihexyloxybenzene (**6**)

To a 2-neck 50 mL round-bottom flask equipped with a N_2 inlet, magnetic stir bar, and reflux condenser was added 215 mg (1.1 mmol) of 4-(trifluorovinyl)benzaldehyde (**2**), 500 mg (0.51 mmol) of compound **4**, and 20 mL of anhydrous THF. The reaction mixture was allowed to stir until all reagents were dissolved, and 284 mg (2.5 mmol) of potassium *t*-butoxide in 7 mL of absolute ethanol was added dropwise. The reaction mixture was then heated to reflux (70°C), and allowed to stir for 24 h. The mixture was cooled to room temperature and 50 mL of CH_2Cl_2 was added. The solution was then extracted with 2×25 mL of concentrated NaCl solution followed by 2×25 mL of water. The organic layer was dried over MgSO_4 and the solvent removed by rotary evaporation. The product was washed repeatedly with MeOH to give 257 mg (74.7% yield) of **6** as a bright yellow powder. ^1H NMR (300 MHz, CDCl_3 , δ): 7.50 (d, $J = 8.6$ Hz, 4H), 7.36–7.07 (m, 9.68H), 6.50–6.67 (m, 0.32H), 4.03 (t, $J = 6.2$ Hz, 3.66H), 3.52 (t, $J = 6.2$ Hz, 0.34H), 1.84 (m, 4H), 1.25–1.37 (m, 12H), 0.875 (s, 6H). ^{19}F NMR (282 MHz, CDCl_3 , δ): –133.7 (dd, $J = 59.2, 111.8$ Hz, 1F), –126.8 (dd, $J = 95.3, 108.5$ Hz, 1F), –119.8 (dd, $J = 59.2, 95.3$ Hz, 1F). Anal. Calcd for $\text{C}_{41}\text{H}_{40}\text{F}_6\text{O}_2$: C, 67.64; H, 5.98; F, 16.89; O, 9.49. Found: C, 67.91; H, 5.79.

2.4. Synthesis of poly(2'-(phenyl)ethenyl)-2,5-dihexyloxybenzene-hexafluorocyclobutane (PFCB-HO-PV)

To a 2-neck 50 mL round-bottom flask equipped with a N_2 inlet, magnetic stir bar, and reflux condenser was added 204 mg (0.51 mmol) of 1,2-bis(4-formylphenoxy)hexafluorocyclobutane (**3**), 500 mg (0.51 mmol) of compound **4**, and 10 mL of anhydrous THF. The reaction mixture was stirred and warmed with a heat gun to dissolve all reagents, and 284 mg (2.5 mmol) of potassium *t*-butoxide in 7 mL of absolute ethanol was added dropwise. The reaction mixture was then heated to reflux (70°C), and allowed to stir for 48 h. The mixture was cooled to room temperature and precipitated into methanol. The solid was isolated by vacuum filtration and precipitated again from THF into MeOH. The precipitate was dried overnight under high vacuum to give PFCB-HO-PV (168 mg, 48.8% yield) as a fluffy yellow solid. ^1H NMR (300 MHz, CDCl_3 , δ): 6.54–7.46 (m, 7H), 4.01–4.02 (br, 2.72H), 3.49–3.55 (br, 1.28H), 1.25–1.84 (m, 16H), 0.899 (s, 6H). ^{19}F NMR (282 MHz, CDCl_3 , δ): –126.70, –127.65, –127.87, –128.33, –128.45, –128.65, –129.47, –130.07, –130.20, –130.74, –130.86, –130.97, –131.39. Anal. Calcd for $\text{C}_{41}\text{H}_{40}\text{F}_6\text{O}_2$: C, 67.64; H, 5.98; F, 16.89; O, 9.49. Found: C, 68.43; H, 6.35.

2.5. Synthesis of poly(2'-(phenyl)ethenyl)-1-methoxy-4-(2-ethylhexyloxy)-hexafluorocyclobutane (PFCB-MEH-PV)

To a 2-neck 50 mL round-bottom flask equipped with a N_2 inlet, magnetic stir bar, and reflux condenser was added 300 mg

(0.74 mmol) of 1,2-bis(4-formylphenoxy)hexafluorocyclobutane (**3**), 703 mg (0.74 mmol) of compound **5**, and 12 mL of anhydrous THF. The reaction mixture was stirred and warmed with a heat gun to dissolve all reagents, and 415 mg (3.7 mmol) of potassium *t*-butoxide in 10 mL of absolute ethanol was added dropwise. The reaction mixture was then heated to reflux (70 °C), and allowed to stir for 48 h. The mixture was cooled to room temperature and precipitated into methanol. The solid was isolated by vacuum filtration and precipitated again from THF into MeOH. The second precipitation followed by drying overnight under high vacuum gave **PFCB-MEH-PV** (232 mg, 44% yield) as a fluffy yellow solid. ¹H NMR (300 MHz, CDCl₃, δ): 6.51–7.48 (m, 14H), 3.72–3.92 (m, 2.25H), 3.31–3.49 (m, 2.75H), 1.46–1.57 (br, 4H), 1.25–1.33 (br, 5H), 0.78–0.89 (m, 6H). ¹⁹F NMR (282 MHz, CDCl₃, δ): –127.55, –128.34, –128.62, –129.31, –129.42, –129.55, –130.06, –130.14, –130.65, –130.92, –131.19, –131.54. Anal. Calcd for C₄₁H₄₀F₆O₂: C, 66.45; H, 5.42; F, 18.02; O, 10.12. Found: C, 67.17; H, 6.03.

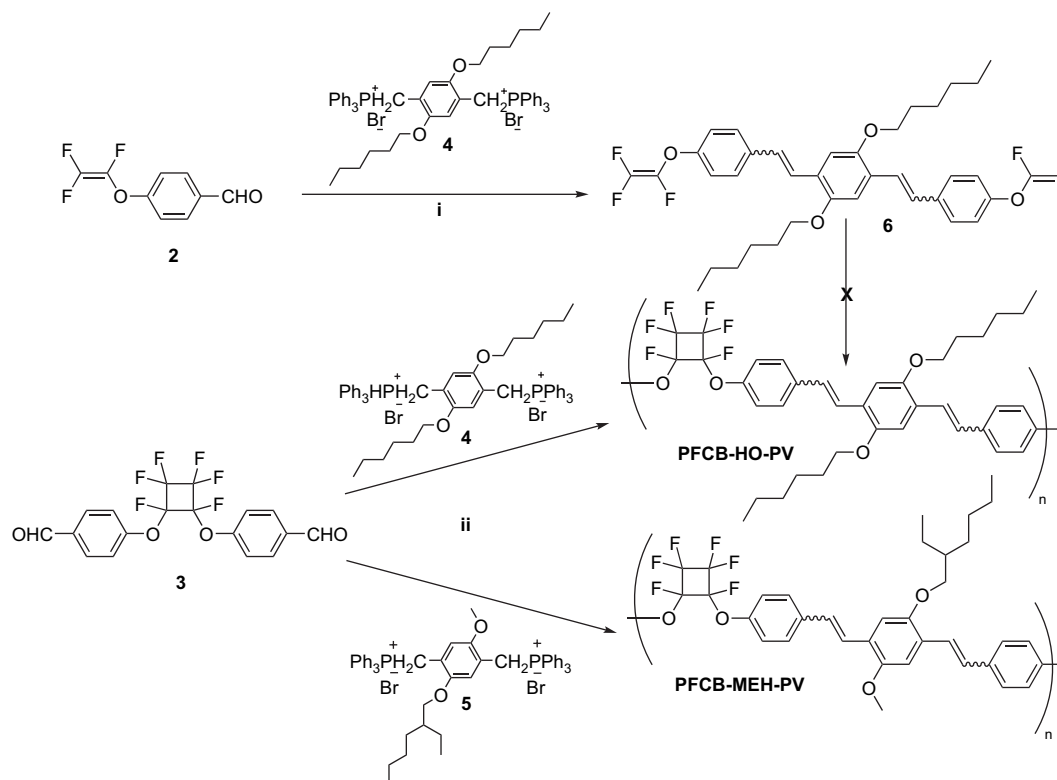
3. Results and discussion

3.1. Synthesis

Starting from commercial 4-bromo(trifluorovinyl)benzene (**1**), metal halogen exchange with *t*-BuLi followed by quenching with *n*-formylmorpholine afforded 4-(trifluorovinyl)benzaldehyde (**2**) in good yield [15]. 4-(Trifluorovinyl)benzaldehyde (**2**) was reacted with 1,4-dihexyloxy-2,5-xylenebis(triphenylphosphonium-bromide) (**4**) under Wittig conditions to yield 1,4-bis(2'-(4-trifluorovinylphenoxy)ethenyl)-2,5-dihexyloxybenzene (**6**) (Scheme 2). Compound **6** was designed as the precursor to PFCB phenylene vinylene polymers. However, subjecting compound **6** to standard PFCB polymerization conditions (170 °C, vacuum sealed ampoule) did not yield the desired PFCB polymer, but rather an insoluble black material was recovered. It has been observed that TFVEs can undergo

cycloaddition reactions to hydrocarbon olefins [18]. In addition to the loss of solubility due to crosslinking, we also observed the loss of chromophore emission. This observation is consistent with the proposed TFVE crosslinking and loss of the stilbene vinyl groups. The inability to thermally polymerize compound **6** does not preclude the formation of PFCB phenylene vinyl materials. By reversing the order in which we form the PFCB linkage, the cross-addition reaction between the TFVE and the stilbene olefin is avoided. 4-Bromo(trifluorovinyl)benzene (**1**) was converted into 1,2-bis(4-bromophenoxy)hexafluorocyclobutane by heating to 170 °C for 20 h. 1,2-Bis(4-bromophenoxy)hexafluorocyclobutane was treated with two equivalents of *t*-BuLi followed by *n*-formylmorpholine to form the 1,2-bis(4-formylphenoxy)hexafluorocyclobutane monomer (**3**) [15]. The PFCB aldehyde monomer was polymerized under Wittig conditions with xylenebis(triphenylphosphoniumbromide) compounds **4** and **5** to yield PFCB linked phenylene vinylene polymers. 1,4-Dihexyloxy-2,5-xylenebis(triphenylphosphonium-bromide) (**4**) and 1-methoxy-4-(2-ethylhexyloxy)-2,5-xylenebis(triphenylphosphoniumbromide) (**5**) were chosen due to similarity to well known PPV materials and for their formation of highly soluble polymers. Wittig polymerization followed by two precipitations from THF into MeOH yielded moderate molecular weight polymers (~8700 M_n) that were soluble in common organic solvents (THF, CH₂Cl₂, acetone, etc.).

The ¹H NMR spectra for **PFCB-HO-PV** and **PFCB-MEH-PV** are shown in Fig. 1. *Cis/trans* stereochemistry of the vinylic linkages results in two broad ¹H NMR signals for the alpha-methylene protons of the pendant alkoxy chains near 4 ppm (*trans*) and 3.5 ppm (*cis*). The presence of two separate signals is attributed to the random stereochemistry of the phenylene vinylene olefin [8] produced by the Wittig reaction. Integration of these signals can be used to calculate the *cis/trans* ratio of the phenylene vinylenes. **PFCB-HO-PV** is 68% *trans* while **PFCB-MEH-PV** contains 45% *trans* olefin.



Scheme 2. Synthesis of phenylene vinylenes containing PFCB polymers. (i) Potassium *t*-butoxide in EtOH, THF, 24 h, 70 °C. (ii) Potassium *t*-butoxide in EtOH, THF, 48 h, 70 °C.

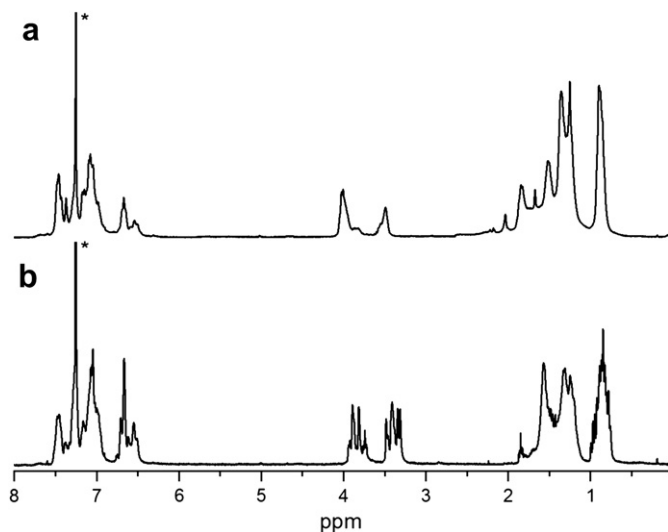


Fig. 1. ^1H NMR spectra of **PFCB-HO-PV** (a) and **PFCB-MEH-PV** (b). The shifts at 3.5 and 4 ppm represent the $-\text{OCH}_2-$ protons and indicate the stereochemistry of the phenylene vinylene olefin. Integration of these signals provides the *cis/trans* ratio for the polymers.

3.2. Thermal characterization

Thermogravimetric analysis at a heating rate of $10^\circ\text{C min}^{-1}$ was used to measure the thermal decomposition of the polymers (Fig. 2). Both polymers exhibited good thermal stability with weight loss not observed until near 400°C , consistent with loss of the alkoxy side chains on the polymers [7]. DSC analysis at $10^\circ\text{C min}^{-1}$ up to 250°C over three heating cycles did not reveal any appreciable thermal transition for either polymer.

3.3. Optical characterization

The optical properties of the materials were measured by solution and solid state absorbance and photoluminescence spectroscopy. **PFCB-HO-PV** and **PFCB-MEH-PV** exhibited a characteristic bimodal absorption in both solution and thin film, with absorption maxima of 392 and 379 nm, respectively (Fig. 3). Fig. 3 also shows photoluminescence measured as a dilute solution in THF; both polymers exhibited similar emission maxima of 445 for **PFCB-HO-PV** and 442 for **PFCB-MEH-PV**. The emission of **PFCB-**

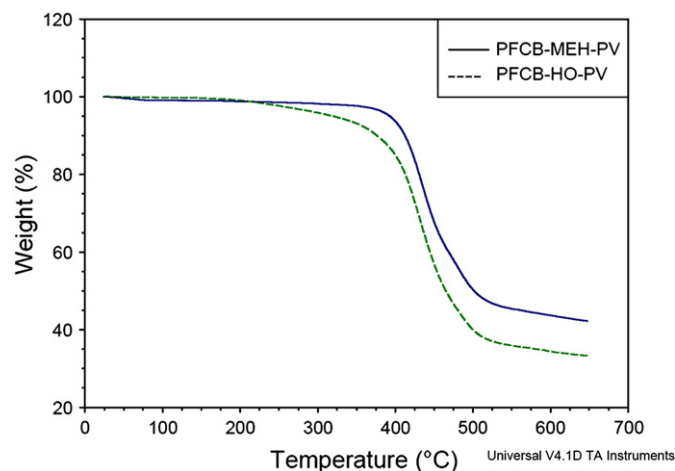


Fig. 2. Thermogravimetric analysis of **PFCB-HO-PV** and **PFCB-MEH-PV** at a heating rate of $10^\circ\text{C min}^{-1}$.

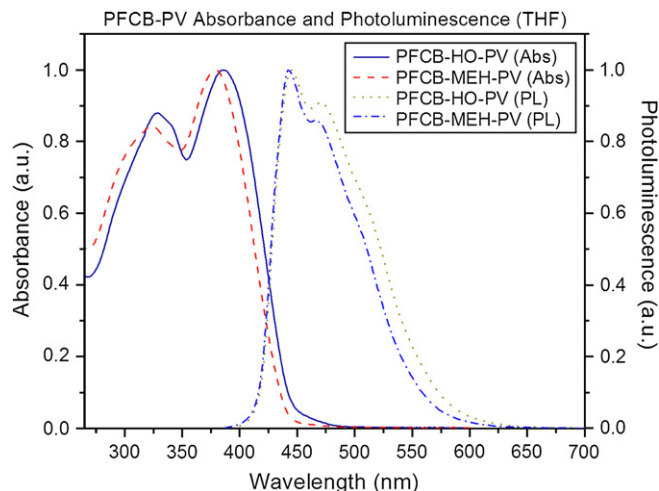


Fig. 3. Solution absorbance and photoluminescence (λ_{max} excitation) of **PFCB-HO-PV** and **PFCB-MEH-PV**.

MEH-PV is blue shifted by nearly 110 nm as compared to commercial MEH-PPV in THF [19]. This is likely due to the reduction of phenylene vinylene conjugation length brought about by the PFCB linkage, and the presence of non-alkoxy substituted benzene rings in the phenylene vinylene chromophore [7].

Solution state quantum yields were calculated for these polymers as compared to quinine sulfate standard. Both polymers exhibited high luminescence efficiencies of 68% for **PFCB-HO-PV** and 71% for **PFCB-MEH-PV**. The solution emission curve and the quantum yield of **PFCB-HO-PV** compare well to the emission of 1,4-bis(2'-phenylethenyl)-2,5-dihexyloxybenzene [8] confirming that the PFCB unit has little electronic effect on chromophore emission.

In order to evaluate the solid state emission of **PFCB-HO-PV** and **PFCB-MEH-PV**, thin films of the materials were spun cast from THF onto a quartz substrate and dried under vacuum overnight. The solid state absorption again showed characteristic bimodality with only a slight red shift observed for both materials compared to solution values (Fig. 4). The photoluminescence of the materials, however, showed a red shift of 40 nm, consistent with the shift seen in 1,4-bis(2'-phenylethenyl)-2,5-dihexyloxybenzene [8]. The **PFCB-MEH-PV** emission in the solid state was blue shifted by nearly 100 nm from commercial MEH-PPV films. This is likely due to several factors: (1) the PFCB linkage reduces chromophore

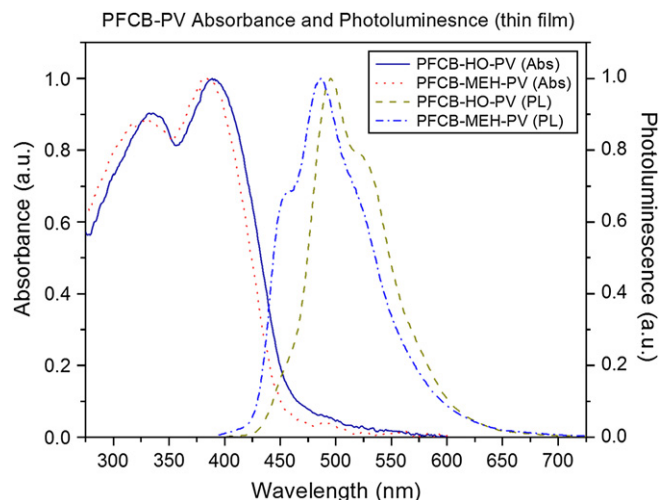


Fig. 4. Solid state absorbance and photoluminescence (λ_{max} excitation) of **PFCB-HO-PV** and **PFCB-MEH-PV** thin films on a quartz substrate.

conjugation length, (2) the presence of non-alkoxy functionalized benzene rings [7], and (3) the random stereochemistry around the PFCB ring and the stereo-irregularity of the phenylene vinylene olefin should prevent stacking of the phenylene vinylene unit. These factors combine to blue shift the emission of the chromophore and increase the bandgap of the polymer [8]. While the emission of the two polymers is similar, the effect of different side chains on the solid state ordering appears as a high energy shoulder on emission spectrum of **PFCB-MEH-PV**.

The optical properties of **PFCB-HO-PV** and **PFCB-MEH-PV** match those that are required for gain layer materials in organic laser diodes [6]. Both polymers exhibit good photoluminescence efficiencies and have high chromophore densities. In addition, the absorbance and photoluminescence spectra show good separation, which is necessary to prevent exciton re-absorption [6]. In addition to the good emissive properties of the new polymers, the optical clarity and thermal stability provided by the PFCB ring should enable them to function well under stimulated emissive conditions.

4. Conclusions

Wittig reaction conditions were used to form two new phenylene vinylenes containing perfluorocyclobutyl aromatic ether polymers and a bis-TFVE-phenylene vinylene monomer. Thermal cyclopolymerization of monomer **6** did not produce the target polymer, so PFCB-aldehyde dimer **3** was used under Wittig conditions to form poly(perfluorocyclobutyl-co-phenylene vinylene) polymers. The polymers exhibited good material properties including excellent thermal stability, high photoluminescence

quantum yields, good separation of the absorption and photoluminescence spectra, and excellent processability. Finally, work is underway to evaluate these polymers for LED emissive layers and as substrates for gain materials in organic light emitting diodes.

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