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Suzuki polycondensation and post-polymerization modification toward electro-optic perfluorocyclobutyl (PFCB) aryl ether polymers: Synthesis and characterization



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1. Introduction

Perfluorocyclobutyl (PFCB) aryl ether polymers are a unique class of amorphous semi-fluorinated polymers, which exhibit a combination of high performance properties such as excellent thermal stability, oxidative stability, chemical resistance, low surface energy, low optical loss, and high electrical insulating ability [1]. As a result, PFCB aryl ether polymers have been utilized in many areas, such as proton exchange membranes (PEMs) in hydrogen–oxygen fuel cells [2], organic nonlinear optic (NLO) host polymers [3–6], organic nanomaterials [7], photonics [8], fire retardant materials, and polymer light emitting diodes [9,10].

Introduction of functionalities into PFCB aryl ether polymers is used to tailor their applications. Functional PFCB aryl ether polymers are traditionally prepared via a [2+2] thermal cyclodimerization of appropriate functional aromatic trifluorovinylether (TFVE) monomers above 150 °C in bulk or in a solution without any catalyst (Scheme 1, Route 1) [11]. Functional TFVE monomers usually are prepared via reactions of their corresponding functional monomer precursors with the mono-functional reactive

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ABSTRACT

Suzuki polycondensation (SPC) as an alternative strategy has been utilized for the first time to readily yield functional perfluorocyclobutyl (PFCB) aryl ether polymers, which are difficult to obtain via the traditional [2+2] thermal cyclopolymerization strategy. Using two reactive PFCB aryl ether molecules as monomers, the biphenyl PFCB aryl ether polymer without any functionality was first prepared and exhibited good thermal stability, up to 450 °C at 8% weight loss (N₂). By choosing appropriate functional monomers, aldehyde-functionalized PFCB aryl ether polymer precursor was also successfully prepared. Post-polymerization modification of this polymer precursor via Knoevenagel condensation yielded three distinct PFCB aryl ether polymers containing thermally stable triarylamine-based electro-optic chromophores.

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TFVE molecules (e.g. p-trifluorovinyl bromobenzene or p-trifluorovinyl benzoic acid, Scheme 1, Route 1). This attractive technology has some limitations. When complex functional structures are required, sometimes it is difficult or impossible to synthesize the corresponding functional TFVE monomers. Direct polymerization of functional TFVE monomers via the [2+2] thermal cyclodimerization cannot always yield desired functional PFCB aryl ether polymers because some functional groups cannot tolerate the high polymerization temperature or may undergo side reactions with TFVE groups during the polymerization process. It has been observed that hydrocarbon olefins (e.g. the double bonds in conjugated NLO chromophores) and aldehyde groups can undergo thermal [2+2] cycloaddition reaction with TFVE groups [12,13].

Alternatively, functional PFCB aryl ether polymers can be prepared via the standard step-growth polymerization of reactive PFCB aryl ether monomers with functional monomers (Scheme 1, Route 2). Reactive PFCB aryl ether monomers are usually prepared from their corresponding mono-functional TFVE molecules via the thermal [2+2] cyclodimerization (Scheme 1, Route 2) [12,14–18]. The synthetic Route 2 has some obvious advantages: functional monomers are much easier to synthesize compared to their corresponding functional TFVE monomers and polymerizations can be performed at much lower temperatures. Up to now, Wittig condensation polymerization [12], the Huisgen's 1,3-dipolar



Scheme 1. Two synthetic routes to synthesize functional PFCB aryl ether polymers.

cycloaddition polymerization [19], nucleophilic aromatic substitution polymerization [18], and palladium catalyzed amination polymerization [15] have been successfully performed to prepare functional PFCB aryl ether polymers via the synthetic Route 2. To our best knowledge, Suzuki polycondensation has not been utilized to prepare functional PFCB aryl ether polymers.

Some electro-optic (EO) chromophore-functionalized PFCB aryl ether thermosetting polymers had been prepared via [2+2] thermal cyclodimerization of their corresponding TFVE monomers (Scheme 1, Route 1) and showed very good EO properties [20,21]. However, no PFCB aryl ether polymer containing thermally stable triarylamine-based EO chromophores is reported in the literatures due to the difficulty in the synthesis of the corresponding functional monomers. In this article, the biphenyl PFCB aryl ether polymer without any functionality was first synthesized via Suzuki polycondensation (SPC in Scheme 2). The properties of the resulting polymer \mathbf{P}_{SPC} were compared to those of a commercially available polymer \mathbf{P}_{TCP} used as a reference. Then PFCB aryl ether polymers containing triarylamine-based chromophores were synthesized via Suzuki polycondensation and post-polymerization modification procedures (Scheme 3). Our results show Suzuki polycondensation is suitable to prepare functional PFCB aryl ether polymers, which allows us to develop many new functional PFCB aryl ether polymers to further broaden their applications.

2. Results and discussion

2.1. Synthesis and characterization of monomers and polymers

Reactive PFCB aryl ethers M1 and M2 were prepared from commercially available mono-functional TFVE molecules via the thermal [2+2] cyclodimerization in good yields (Scheme S1) [22], whose structures were confirmed by ¹H NMR and ¹⁹F NMR spectra. Suzuki polycondensation of these two monomers afforded a biphenyl PFCB aryl ether polymer P_{SPC} in a good yield (71%), which is analogous to the commercially available biphenyl PFCB aryl ether polymer P_{TCP} prepared via the thermal [2+2] cyclodimerization polymerization process. The number-average molecular weight (M_n) for purified polymer **P**_{SPC} was determined to be 5400 g/mol with a polydispersity index (PDI) of 1.7 by size exclusion chromatography (monodisperse polystyrene standards, THF as the eluent). The structure of polymer P_{SPC} was probed by ¹⁹F NMR spectroscopy, which displayed characteristic PFCB spectroscopic patterns as seen in P_{TCP} (Fig. 1). The ATR-FTIR spectrum of **P**_{SPC} shows a broad, strong absorbance of the PFCB ring breathing mode appeared at 960 cm⁻¹ (Fig. S1). Both ¹⁹F NMR and ATR-FTIR results indicated that the PFCB ring in the monomers did not participate in significant side reactions during Suzuki polycondensation process. Polymer PSPC has different end groups with polymer P_{TCP} (Scheme 2). The end groups of polymer P_{TCP} are aryl TFVE groups shown in its ¹⁹F NMR spectrum (the characteristic pattern at \sim -119, -126, and -134; Fig. 1). Polymer **P**_{SPC} has two different end groups: the bromine end group and the boronate ester end group (Scheme 2). The ¹H NMR spectrum of polymer P_{SPC} shows a small signal at 1.26 ppm, which is associated to the hydrogen atoms of boronic perco-ester end groups (Fig. S2). The results from thermogravimetric analyzer/mass spectrometer (TGA-MS) studies show that polymer P_{SPC} also contains some bromine end groups (Fig. S6). Due to containing two different end



Scheme 2. Two synthetic routes to biphenyl PFCB aryl ether polymers: Suzuki polycondensation (SCP) and thermal [2+2] cyclodimerization polymerization (TCP). End groups (X) vary as a function of the polymerization route.



Scheme 3. The synthetic route to PP via Suzuki polycondensation and P1-P3 via post-polymerization modification.

groups, the molecular weight of polymer P_{SPC} cannot be determined from end-group analysis by NMR.

To obtain electro-optic (EO) chromophore-functionalized PFCB aryl ether polymers, the EO chromophore precursor-functionalized monomer **M3** (Scheme 3) was synthesized by following previously published procedures (Scheme S1) [23] and its structure was confirmed by ¹H NMR (Fig. S8) and ¹³C NMR spectroscopy. Copolymerization of monomers **M1–M3** afforded an aldehyde-appended PFCB aryl ether polymer precursor **PP** in a good yield (Scheme 3). In this polymerization reaction, feed molar ratios of **M1**, **M2** and **M3** (40:50:10) were controlled in order to obtain a polymer with a desired chromophore loading (around 10%). The actual chromophore loading of the resulting polymer **PP** was determined from its ¹H NMR spectrum. Integration ratio between the aldehyde proton and biphenyl protons is 1:10.



Fig. 1. ¹⁹F NMR spectra for P_{TCP} (top) and P_{SPC} (bottom). TFVE end groups, present in P_{TCP} , are absent in P_{SPC} , however, PFCB structure (-128 to -131 ppm) is present in both P_{TCP} and P_{SPC} , confirming the similar product from the two separate polymerization routes.

The final triarvlamine-based EO chromophore-functionalized polymers P1-P3 were prepared using post-polymerization modification via Knoevenagel condensation reactions of the aldehvdefunctionalized polymer precursor **PP** with three different electron acceptors: 1,3-diethyl-2-thiobarbituric acid (BBA), 2-(3-cyano-4,5,5-trimethyl-5H-furan-2-ylidene)malononitrile (TCF), and malononitrile (MA), respectively (Scheme 3). The signal of the aldehydic proton in polymer **PP** at 9.91 ppm is absent in the spectra of the final functional polymers P1-P3, meanwhile, signals of olefinic protons connecting with electron acceptors appear at 8.64 ppm for **P1** and 8.09 ppm for **P2**, confirming the formation of the full conjugated EO chromophores on the side chains (Fig. S3). For P3, the signals of olefinic protons are obscured by the signals of backbone aromatic protons and are hard to identify (Fig. S3). The integration ratio of the double bond proton, which was close to the electron acceptor group BBA, and biphenyl protons from the ¹H NMR spectrum of P1 is determined to be 1:10 (Fig. S4). The percentage of chromophore in final polymer P1 did not change compared to that of the polymer precursor PP, indicating the polymer matrix is inert and compatible with this mild postpolymerization modification condition.

The physical properties of the commercially available PFCB aryl ether polymer P_{TCP} used as a reference and the resulting PFCB aryl ether polymers P_{SPC} , **PP**, and **P1–P3** are summarized in Table 1. As shown in Table 1, the molecular weights of the resulting polymers P_{SPC} , **PP**, and **P1–P3** were relatively low and oligomeric in nature. The increased number-average molecular weights (M_n) and decreased PDIs of **P1–P3** compared to **PP** are attributed to the purification employed after post-polymerization modification, which removed fragments with lower molecular weights. The resulting polymers **P_{SPC}**, **PP**, and **P1–P3** exhibit excellent solubility in various organic solvents such as chlorobenzene, acetone, chloroform and THF.

2.2. Thermal properties

The thermal properties of polymer P_{SPC} were investigated via DSC and compared to polymer P_{TCP} (Fig. S5). Whereas polymer P_{TCP} had a glass transition at 130 °C, polymer P_{SPC} has a

Entry	M _n (g/mol)	M _w (g/mol)	PDI	$T_{\rm d}^{\rm onset}$ (°C)	T_{g} (°C)	$E_{1/2}$ (eV)	$E_{\rm ox}^{\rm a} ({\rm eV})$	$\lambda_{onset}^{b}(nm)$	$E_{\rm gap}^{c} (eV)$	$E_{\rm HOMO}^{\rm d}$ (eV)	E_{LUMO}^{e} (eV)
P _{TCP}	24,000	44,000	1.8	450	130	-	-	_	_	-	-
P _{SPC}	5400	9200	1.7	245	109	-	-	-	-	-	-
PP ^f	3600	8500	2.4	220	93	0.48	0.36	500	2.48	5.16	2.68
P1 ^f	5700	7100	1.3	230	130	0.47	0.33	668	1.86	5.13	3.37
P2 ^f	5500	6900	1.3	206	128	0.43	0.33	754	1.64	5.13	3.49
P3 ^f	4500	6000	1.3	200	110	0.47	0.27	613	2.02	5.07	3.05

Molecular weights and thermal properties of the PFCB aryl ether polymers.

^a E_{0x} taken from the straight line approximation of the onset of oxidation in the CV voltammogram.

^b λ_{onset} taken from the straight line approximation of the onset of absorption in the UV-vis spectrum.

^c E_{gap} estimated from λ_{onset} , $E_{\text{gap}} = 1240 \text{ nm} \cdot V / \lambda_{\text{onset}}$.

^d $E_{HOMO} = E_{ox} + 4.8$.

^e $E_{\text{LUMO}} = E_{\text{HOMO}} - E_{\text{gap}}$

^f 10 wt% chromophore.

significantly lower glass transition at 109 °C due to a much lower number-average molecular weight of the polymer chains of **P**_{SPC} compared to **P**_{TCP}, 5400 and 24,000, respectively (Table 1). The aldehyde-functionalized polymer precursor **PP** exhibits the lowest glass transition temperature (around 93 °C). The three full EO chromophore-functionalized PFCB aryl ether polymers **P1–P3**, have relatively higher $T_{\rm g}$ s.

The thermal stability and degradation byproducts of polymer **P**_{SPC} and polymer **P**_{TCP} were probed by TGA (Fig. 2) and TGA–MS (Fig. S6) techniques. The TGA thermogram of polymer P_{SPC} shows a two-step degradation process (Fig. 2). The first step degradation process mainly takes place at around 250 °C, the second step degradation takes place at around 450 °C. For the first step degradation. TGA-MS results show a loss of bromobenzene (156 amu and 158 amu) and a loss of benzene ring (78 amu). which suggests the major weight loss (around 8% weight loss) of polymer P_{SPC} from 220 °C to 300 °C comes from the degradation of a large amount of the bromobenzene end group due to its low molecular weight. For the second step degradation, TGA-MS results show polymer P_{SPC} has the same mass fragmentation pattern as polymer P_{TCP} at the temperatures of 450 °C and on. These mass fragments of the second step degradation showed a good agreement with previously reported literature values of degradation of common PFCB aryl ether polymers [24]. The main mass fragments are listed at 93 amu which corresponds to a phenol, then at 162 amu corresponding to a hexafluorocyclobutane ring. Over all, the polymer P_{TCP} has good thermal stability up to 450 °C with 8% weight loss (bromobenzene end groups) in an inert atmosphere.

The polymer precursor **PP** has a huge weight loss (\sim 30%) from 200 °C to around 450 °C (Fig. 2) and exhibits much less thermal stability compared to the polymer **P**_{SPC} due to the degradation of the aldehyde pending chromophore precursors on the side chains [13,25,26]. The final EO chromophore-functionalized polymers

P1–P3 have similar degradation patterns (two step degradation) with the polymer **P**_{SPC} and a slightly larger weight loss (~15%) during the first step degradation. The reduced thermal stability of the functional polymers **P1–P3** compared to the polymer **P**_{SPC} is due to the degradation of the side-chain EO chromophores (the chromophores begin to degrade at 250 °C) [13,25,26], and some impurities (unreacted acceptors) in the samples.

2.3. Optical and electrochemical properties

The absorption spectra of the resulting polymers PP and P1-P3 were measured in dilute chloroform (1 g/L) (Fig. 3). The polymer solutions are shown in Fig. 3, and reveal significant contrasts in color: yellow (PP), purple (P1), blue (P2) and orange (P3). All these four polymers exhibit three or four major absorption bands in the UV-vis spectra. The first strongest absorption peak at ~260 nm is followed by a weaker absorption ~350 nm, these peaks correspond to the π - π ^{*} transition of biphenyl and conjugated chromophore side chains, respectively. Further absorbance is correlated to the intramolecular charge transfer (ICT) from the triphenyl amino groups $(n-\pi^*)$ in the main chain to the acceptor groups or aldehyde group in the pendent side chains. The lowest energy ICT absorption peaks of PP (aldehyde), P1 (BBA), P2 (TCF), and P3 (MA) are 430 nm, 570 nm, 619 nm, and 517 nm, respectively. This trend matches the strength of the electron acceptor groups. The stronger electron acceptors produce the larger the absorption peaks in the absorption spectra.

The electronic structures of the resulting polymers **PP** and **P1–P3** were studied by cyclic voltammetry and UV–vis techniques to explore their potential applications in photonic systems. While the half wave potentials ($E_{1/2}$) for these four polymers were fairly similar, ±0.03 V, their redox couple resided ~0.2 V more anodic than analogous single molecule chromophores (Table 1 and Fig. S7)



Fig. 2. Thermograms of PFCB aryl ether polymers PSPC, PTCP, PP, and P1-P3.



Fig. 3. UV-vis absorption spectra and picture of polymer (PP and P1-P3) solutions in chloroform.

[13]. The increase in the oxidation potential suggests a decrease in the electronic density of the donor functionality due to the substitution and conformation effects on triarylamine-based electron donors (RO-phenyl- vs. –OCH₃) [27].

The band gaps of the full EO chromophore-functionalized polymers were measured by UV-vis spectroscopy by taking the onset of absorption of lowest energy transition in each polymer and converting it to electron volts. Good correlation was found between the strength of the acceptor groups and the extent of the bathochromic shifts (from **PP**), with stronger groups producing larger shifts in E_{gap} (from 1.64 to 2.48 V).

Additionally, the highest occupied molecular orbital (HOMO) energies and lowest unoccupied molecular orbital (LUMO) energies were obtained utilizing the onset of oxidation in the CV as an anchor point (Table 1), correcting to vacuum and subtracting the approximated band gap. While a little change in the HOMO was observed across the series (0.09 V), substantial variation in the LUMO (0.81 V) was seen as a function of the strength of electron acceptor groups.

3. Conclusion

Suzuki polycondensation for the first time has been successfully utilized to prepare a PFCB aryl ether polymer P_{SPC} without any functionality and an aldehyde-functionalized PFCB aryl ether polymer precursor **PP**, which is difficult to synthesize via [2+2] thermal cyclodimerization due to the reaction of the aldehyde groups with TFVE groups at high temperatures. The polymerizations were performed at a much lower temperature (80 °C) than the required high polymerization temperatures $(>150 \,^{\circ}C)$ for traditional synthetic route via [2+2] thermal cyclodimerization, which allows us to prepare more functional PFCB aryl ether polymers. The physical properties of P_{SPC} have been compared to the literature and commercial standard. The polymer P_{SPC} maintains good thermal stability of PFCB aryl ether polymer. The decrease in thermal stability is mainly due to the less thermally stable bromobenzene end groups presenting in polymer **P**_{SPC}. Further, the full triarylamine-based chromophore-functionalized PFCB aryl ether polymers P1-P3 were successfully prepared by post-polymerization modification via Knoevenagel condensation of PP with different electron acceptors. The advantage of this method is that three EO polymers are obtained from just one polymer precursor. These three polymers exhibit high solubility and good thermal stability. Future works will focus on improving the molecular weight of the PFCB aryl ether polymers prepared via Suzuki polycondensation, increasing their thermal stability by removing the potentially reactive bromo and boronic ester functionalities through end capping, incorporating more functional groups into PFCB aryl ether polymers to extend their applications.

4. Experimental

4.1. Materials

4-(1,2,2-Trifluorovinyloxy) phenylboronic acid and 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan2-yl)-phenyl trifluorovinyl ether were donated by and are commercially available from Tetramer Technologies, LLC and distributed though Oakwood Chemicals, Inc. 2-(2-{4-[N,N-Di(4-bromophenyl]amino]phenyl}ethenyl)thien-5-al (**M3**) (Scheme S1) [23] and 2-(3-cyano-4,5,5-trimethyl-2(5*H*)-furanylidene)-propanedinitrile (TCF) were synthesized according to published procedure [28]. 1,2-Bis(4-bromophenoxyl)hexafluor-ocyclobutane (**M1**) and 1,2-bis{4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan2-yl)phenoxyl}henxafluorocyclobutane (**M2**) were prepared from their corresponding TFVE monomers according to published procedures (Scheme S1) [22]. For comparative purposes,

commercial BP-PFCB polymer (hereafter P_{TCP}) purchased from Tetramer Technologies, LLC was used as a reference material. All other reagents were purchased from Aldrich or Alfa Aesar and used without further purification.

4.2. Analysis

¹H. ¹³C and ¹⁹F NMR spectra were recorded on a Bruker 400 or 500 MHz NMR and chemical shifts were measured in ppm (δ) with reference to an internal standard: tetramethylsilane (0 ppm), deuterated chloroform (77 ppm), and trichlorofluoromethane (0 ppm) for ¹H, ¹³C and ¹⁹F NMR, respectively. ATR-FTIR was recorded on a Shimadzu IR-Affinity 1 in ATR module with a germanium probe. Experiments were tested in transmission mode at a resolution of 4.0 measuring between 700 cm^{-1} and 4000 cm^{-1} for 32–72 scans. Ultraviolet-visible absorption spectra were measured using an Agilent 8453 UV-vis spectroscopy system. Differential scanning calorimetry (DSC) analysis was performed on a Mettler Toledo DSC 1 system under nitrogen at a heating rate of 10 °C/min. The glass transition temperature (T_g) was obtained from a second heating cycle using Star E version 10.0 software suite. Thermal gravimetric analysis (TGA) was performed on a Mettler-Toledo TGA/ DSC 1 LF instrument under nitrogen at a heating rate of 10 °C/min up to 800 °C. Thermogravimetric analysis with mass spectroscopy (TGA-MS) was performed on a Mettler TGA/DSC-1 and a Pfeiffer PrismaPlus QMG-220 as the mass spectrometer. The TGA method was set with a rate of 5 °C/min from 30 °C to 800 °C while scanning the mass spectrometer from 30 amu to 200 amu simultaneously. The results were then imported into Origin for data analysis. Gel permeation chromatography (GPC) data were collected in THF from a Waters 2690 Alliance System with photodiode array detector. GPC samples were eluted in series through Polymer Labs PLGel 5 mm Mixed-D and Mixed-E columns at 35 °C. Molecular weights were obtained using polystyrene as a standard (Polymer Labs Easical PS-2). Electrochemical measurements were performed in a 0.1 M solution of electrochemical grade tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in dichloromethane. All samples were gently purged with nitrogen prior to scanning and run under an inert atmosphere (note: purging must be gentle to avoid solvent evaporation and change in electrolyte concentration). Cyclic voltammetry was carried out on a BASi CV-50W analyzer with a platinum working electrode, platinum wire auxiliary electrode, and Ag/AgCl reference electrode. Samples were calibrated to the Fc/Fc⁺ couple.

4.3. Synthesis of PSPC

1,2-Bis{4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan2-yl)phenoxyl}hexafluorocyclobutane (**M2**) (348 mg, 0.6 mmol) and 1,2bis(4-bromophenoxyl)hexafluorocyclobutane (**M1**) (291 mg, 0.6 mmol) were placed into a 50 mL two-neck round-bottom flask. A mixture of 2 M K₂CO₃ aqueous solution (2 mL) and THF (20 mL) were added into the flask and the reaction mixture were degassed followed by the addition of a catalytic amount of Pd(PPh₃)₄ (66 mg, 0.06 mmol). The reaction mixture was then refluxed with vigorous stirring for 72 h under an N₂ atmosphere. The reaction mixture was cooled to room temperature, and then was poured into methanol (100 mL) and the resulting light yellow precipitate was collected through vacuum filtration and washed sequentially with D.I. water, MeOH, and hexanes. The solid polymer was then dried in a vacuum oven at 60 °C for an additional 24 h to afford **P**_{SPC} as a light yellow powder (285 mg, 71%).

¹H NMR (500 MHz, CDCl₃) δ 7.49 (s, 4H), 7.23 (dd, *J* = 28.8, 6.9 Hz, 4H), 1.31 (d, *J* = 31.1 Hz, 2H), 0.99–0.78 (m, 1H). ¹⁹F NMR (471 MHz, acetone-*d*₆) δ –127.5 (s), –129.5 (s), –120.0 (s), –130.6 (s), –130.8 to –131.5 (m), –131.3 (s), –131.5 (s), –131.8 (s).

4.4. Synthesis of PP

To a 25 mL two-neck round-bottom flask containing 1,2-bis (4hexafluorocyclobutane (307 mg. bromo-phenoxyl) (M1) 0.6 mmol), 1,2-bis (4-boro-perco-ester-phenoxyl) hexafluorocyclobutane (M2) (600 mg, 1 mmol), and 2-(2-{4-[N,N-di-(4-bromophenvl) aminolphenvl}ethenvl)thien-5-al (**M3**) (210 mg. 0.4 mmol) was added 13 mL of a base/solvent mixture (3:10. 2 M K₂CO₃ (aq):THF), after which the reaction mixture was degassed followed by the addition of a catalytic amount of Pd(PPh₃)₄ (21 mg, 0.018 mmol). The reaction mixture was then refluxed with vigorous stirring for 72 h under an N₂ atmosphere. The reaction mixture was then cooled and poured into MeOH (100 mL), after which the resulting yellow precipitate was collected through filtration and washed sequentially with D.I. H₂O and hexanes. The solid polymer was then dried in a vacuum oven at 60 °C for an additional 24 h to afford PP as a yellow powder (800 mg, 80%). ¹H NMR (400 MHz, CDCl₃) δ 9.91 (s, CHO), 7.89 (s), 7.82–7.02 (m), 6.97 (s); ¹³C NMR (101 MHz, acetone- d_6) δ 152.1, 151.8, 137.3, 137.0, 134.7, 133.2, 133.1, 129.9, 128.6, 128.5, 127.9, 119.0, 118.6; 19 F NMR (376 MHz, CDCl₃) δ –126.1, –127.3, –127.5, -128.0, -128.1, -128.9, -129.5, -129.6, -130.2, -130.4, -130.7, -130.9, -131.1; ATR-FTIR (cm⁻¹) v 1669, 1602, 1493, 1301, 1264, 1196, 1170, 1115, 1006, 958, 822.

4.5. Synthesis of P1

Triethvlamine (0.1 mL, 0.7 mmol) was added in excess to a solution of **PP** (200 mg, 0.06 mmol) and 1.3-diethyl-2-thiobarbituric acid (100 mg, 0.65 mmol) in 2 mL methylene chloride in a two-neck 10 mL round-bottom flask. The solution was then stirred at room temperature under N₂ atmosphere for 24 h, and then poured into methanol (100 mL). The precipitate was filtered off and washed with water, methanol, and hexane. The solid polymer was then dried in a vacuum oven at 70 °C for 24 h to afford P1 as a purple powder (208 mg, 90%). ¹H NMR (400 MHz, CDCl₃) δ 8.64 (s, -CH=C-), 7.81 (s), 7.71-7.00 (m), 4.68-4.56 (m, -CH₂-), 1.42-1.31 $(m, -CH_3)$; ¹³C NMR (100 MHz, CDCl₃) δ 152.1, 152.0, 137.2, 137.0, 132.8, 132.7, 128.3, 128.2, 127.9, 118.8, 118.4; ¹⁹F NMR (400 MHz, $CDCl_3$) δ -126.0, -127.4, -127.5, -128.0, -128.1, -128.9, -129.5, -129.6, -129.7, -130.2, -130.3, -130.4, -130.7, -130.9, -131.0;ATR-FTIR (cm⁻¹) v 1662, 1602, 1552, 1493, 1391, 1301, 1265, 1198, 1167, 1116, 1006, 959, 822.

4.6. Synthesis of P2

PP (62 mg, 0.07 mmol) and 2-(3-cyano-4,5,5-trimethyl-5H-furan-2-ylidene) malononitrile (66 mg, 1.15 mmol) were used via the same procedure outlined for the preparation of **P1** to afford **P2** as a dark blue powder (50 mg, 74%). The product was characterized by ¹H NMR (400 MHz, CDCl₃) δ 8.09 (s, -CH=C-), 7.80 (s), 7.76 (s), 7.50 (d, *J* = 4 Hz), 7.26 (d, *J* = 4 Hz), 7.20 (d, *J* = 4 Hz), 7.15–7.01 (m), 6.64 (d, *J* = 8 Hz), 1.79 (d, *J* = 6.5 Hz, $-CH_3$); ¹³C NMR (101 MHz, CDCl₃) δ 152.1, 152.0, 137.2, 137.0, 130.8, 128.3, 128.2, 119.0, 118.9, 118.4, 116.2, 115.6, 27.1, 26.8; ¹⁹F NMR (376 MHz, CDCl₃) δ -125.3, 126.1, -127.4, -127.5, -128.0, -128.1, -128.8, -128.9, -129.1, -129.6, -130.2, -130.4, -130.7; ATR-FTIR (cm⁻¹) ν 2227, 1658, 1604, 1559, 1494, 1437, 1397, 1378, 1304, 1264, 1196, 1171, 1111, 1006, 959, 900, 851, 822.

4.7. Synthesis of P3

PP (50 mg, 0.06 mmol) and malononitrile (50 mg, 0.65 mmol) were used via the same procedure outlined for the preparation of **P1** to afford **P3** as an orange powder (40 mg, 75%). ¹H NMR (400 MHz, CDCl₃) δ 7.75 (s, -CH=C-), 7.70 (s), 7.68 (s), 7.50 (d,

 $J = 4 \text{ Hz}), 7.43 \text{ (d, } J = 4 \text{ Hz}), 7.26 \text{ (d, } J = 4 \text{ Hz}), 7.20 \text{ (d, } J = 4 \text{ Hz}), 7.15 \text{ (s)}, 7.10 \text{ (d, } J = 4 \text{ Hz}), 7.08-7.05 \text{ (m)}; {}^{13}\text{C} \text{ NMR} (101 \text{ MHz}, \text{CDCl}_3) \delta$ 161.1, 152.1, 152.0, 137.2, 136.9, 134.5, 134.1, 132.8, 130.8, 128.3, 128.2, 128.0, 119.0, 118.8, 118.5, 116.2, 115.6; {}^{19}\text{F} \text{ NMR} (376 \text{ MHz}, \text{CDCl}_3) \delta -125.1, -127.4, -127.5, -128.0, -128.1, -128.3, -128.8, -128.9, -129.0, -129.5, -129.6, -129.7, -130.2, -130.4, -130.7; ATR-FTIR (cm⁻¹) ν 2219, 1604, 1493, 1435, 1396, 1303, 1264, 1194, 1167, 1116, 1007, 956, 899, 822.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jfluchem.2015. 10.004.

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