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Synthesis of Poly(arylenevinylene)s with Fluorinated Vinylene Units

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Poly(arylenevinylene) polymers bearing fluorine atoms in the vinylene units were obtained by a Stille cross-coupling reaction of (*E*)-(1,2-difluoro-1,2-ethenediyl)bis(tributylstannane) with diiodoaryl derivatives. The introduction of fluorine atoms on the double bond of the stannane leads to polymers with relatively high molecular weights. Furthermore, the presence of fluorinated vinylene units changes the optical properties of the polymers and shifts the emission towards the blue region of the visible spectrum. A fluorinated analogue of MEH-PPV was obtained, and it shows photoluminescence that is considerably blueshifted, also in the solid state, relative to that found for nonfluorinated MEH-PPV and to other PPVs with fluorinated double bonds.

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Introduction

Poly(*p*-phenylenevinylene)s (PPVs) represent one of the most widely investigated classes of conjugated polymers for organic electronics, and their application in organic light-emitting diodes (OLEDs), lasers and photovoltaic cells have been reported.[1] The introduction of substituents into different positions of the main conjugated backbone enables fine-tuning of the electrical and optical properties of this class of polymers through steric and electronic effects. These effects can also be exploited, in many cases, to control the supramolecular aggregation of these materials in the solid state.[2] Among the three principal colours necessary for applications in light-emitting displays, high-efficiency green and red emission can be obtained readily from PPV derivatives, whereas efficient blue-emitting PPVs are difficult to obtain. A blueshift in the absorption and emission spectra of PPV polymers has been achieved mainly by introduction of sterically hindering substituents in the appropriate positions,[3] which served to reduce the effective conjugation length by twisting the conjugated π systems.

Functionalization of PPVs with electron-withdrawing groups has also been systematically investigated as a possible approach to widen the energy gap.[4] The introduction of electron-withdrawing groups on the PPV backbone has also been shown to lower the HOMO and LUMO energies, which improves the electron-transportation properties of the polymer; in turn, this makes electron injection easier from a high work function cathode in electroluminescent devices. By using this approach, it is possible to simplify the architecture of the OLED device, which thus avoids the introduction of an organic electron-injecting layer. Fluorine atoms and fluorinated groups have been investigated as effective electron-withdrawing substituents that are able both to increase the electron affinity and to blueshift the emission in various classes of electroluminescent conjugated compounds.[5] In the case of PPVs, the approach more frequently adopted consists of introducing fluorine atoms onto the aromatic rings, whereas their introduction into PPV vinylene units is synthetically more demanding. In fact, previously, only two PPV polymers bearing fluorinated vinylene units were reported by Suh and coworkers.[6] The Gilch methodology used in their report for the preparation of poly(*p*-phenylenedifluorovinylene) (PPDFV) and poly(2-dimethyloctylsilyl-*p*-phenylenedifluorovinylene) (DMOS-PPDFV) is based on the treatment of the monomers with strong bases. However, this prevents the extension of the procedure to base-sensitive functionalized substrates. Furthermore, incomplete elimination of halogen atoms and coupling in a head-to-head or tail-to-tail fashion represent common drawbacks of the Gilch approach.[7] This can lead to defects in the conjugated polymers and, in principle, limit the use of this reaction as a general methodology for the synthesis of poly(arylenedifluorovinylene)s.

In previous work, we reported several synthetic methodologies based on organometallic reactions for the synthesis of functionalized polyconjugated materials,[8]and in particular, several poly(*p*-phenylenevinylene)s were obtained by the

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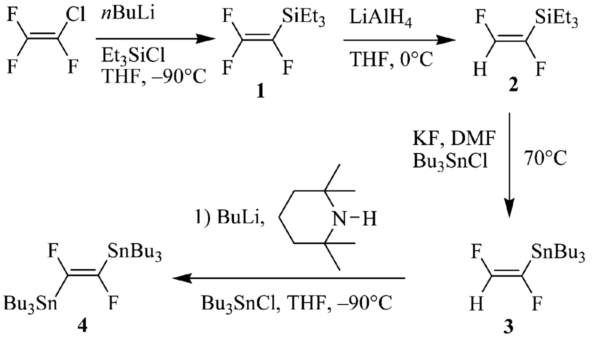
Stille cross-coupling reactions of suitable phenylene bis(halide)s and (*E*)-1,2-bis(tributylstannyl)ethene.[9a,9b] This protocol was convenient and straightforward; it afforded relatively low molecular weight polymers with a high degree of regio- and stereoregularity and no conjugation defects. PPVs bearing fluorine atoms on the aromatic rings were also obtained by this approach.[5e,5f] The availability of (*E*)-(1,2-difluoro-1,2-ethenediyl)bis(tributylstannane), as reported by Burton et al.,[10] prompted us to extend our Stille-based methodology to PPVs with fluorinated double bonds. Our experiments resulted in a general and convenient protocol that we report in this paper.

Results and Discussion

The organometallic monomer (*E*)-(1,2-difluoro-1,2-ethenediyl)bis(tributylstannane) was synthesized following the sequence shown in Scheme 1, and this method displays significant improvements with respect to the route reported in the literature.[10]

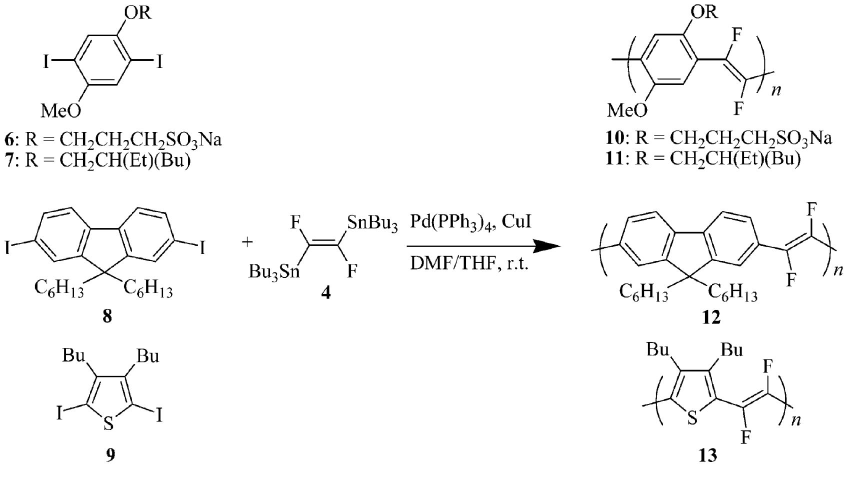


Scheme 1. Synthetic approach used for the synthesis of organometallic reagent **4**.

The first modification is represented by the use of chlorotriethylsilane as a reagent in place of chlorotrimethylsilane to obtain intermediates **1** and **2**. Compounds **1** and **2** have relatively high boiling points and can be purified easily by distillation. The same purification is not possible when chlorotrimethylsilane is used, because the resulting intermediates have boiling points similar to those of the reaction solvents. As a second modification to the literature protocol, we found that it was more convenient to perform the transmetallation process with reagents such as tributyltin chloride and potassium fluoride in DMF, in place of tetrabutylammonium fluoride and bis(tributyltin)oxide in THF. The silicon–tin exchange was carried out at 70 °C and product **3** was isolated by distillation. The last step was performed by following a literature procedure, but simple distillation was possible instead of chromatography for the purification of compound **4**.

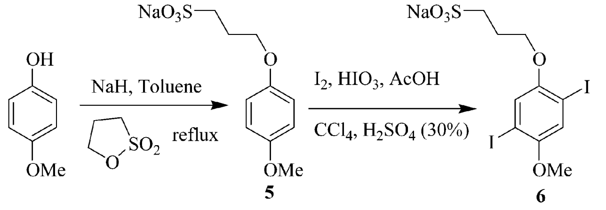
To explore the scope and limitations of the polymerization protocol proposed, we investigated the reactivity of **4** with a series of diiodoaryl derivatives, such as 1,4-diiodobenzenes **6** and **7** bearing alkoxy substituents in the 2- and 5-positions, 9,9-dialkylfluorene diiodide **8** and 2,5-diiodothiophene **9** bearing two alkyl groups in the 2- and 3-positions (Scheme 2).

The copolymerization of **4** with monomers **6**–**9** afforded polymers **10**–**13** (Scheme 2), which represent the fluorinated counterparts of several poly(arylenevinylene)s that are of great interest in many areas, including the field of electroluminescent devices. Polymer **11** is an analogue of MEH-PPV, which is one of the most widely used red-emitting PPV derivatives in electroluminescent devices.[11] Polyfluorenevinylenes, of which polymer **12** is a fluorinated counterpart, are also promising materials for light-emitting diodes, and they show emission that is shifted to shorter wavelengths with respect to that of MEH-PPV.[12] On the contrary, poly(thienylenevinylene)s are low bandgap materials,[13] and polymer **13** is the fluorinated representative of this class of conjugated polymers. Finally, polymer **10** belongs to the polyelectrolyte class of PPV derivatives,[14] which are potential active materials in light-emitting cells (LECs) – a more recent type of electroluminescent device.[15] In all cases, the introduction of fluorine atoms on the double bond is expected to modify, as discussed above, the emissive properties of these polymers with respect to the corresponding nonfluorinated materials.



Scheme 2. Synthetic route for the preparation of poly(arylenevinylene)s with fluorinated vinylene units.

The general synthetic protocol for the preparation of polymers **10**–**13** (Scheme 3) is based on the Stille cross-coupling reaction of equimolar amounts of (*E*)-(1,2-difluoro-1,2-ethenediyl)bis(tributylstannane) (**4**) and diiodoaryls **6**–**9**, in the presence of $Pd(PPh_3)_4$ as a catalyst, CuI in a stoichiometric amount and a THF/DMF mixture as the solvent. All the polymerization reactions proceeded at room temperature and were complete after one week. Polymer **10** was purified by crystallization from DMF/acetone and obtained as a yellow-green powder. Polymers **11** and **12** were isolated by washing the crude product, with the aid of a Soxhlet apparatus, with hexane (24 h) and ethanol (24 h) and then by extracting the residual material with chloroform. Evaporation of the solvent under reduced pressure afforded pure polymers **11** and **12** as green and light-green powders, respectively. In the case of polymer **13**, dichloromethane was used for the Soxhlet extraction. After concentrating the solution, methanol was added to produce a dark-red precipitate. Finally, the pure product was obtained by recrystallization from dichloromethane/methanol.



Scheme 3. Synthetic route for the preparation of monomer **6**.

Monomers **7**,[16] **8**[17] and **9**[18] were synthesized as reported in the literature, whereas diiodoaryl monomer **6** was obtained as described in Scheme 3.

4-Methoxyphenol and sodium hydride were allowed to react with 1,3-propanesultone in toluene at reflux. Pure product **5** was obtained after purification by crystallization from DMF/acetone and then submitted to iodination by using I_2/HIO_3 in carbon tetrachloride, acetic acid and sulfuric acid (30%). Monomer **6** was purified by crystallization from DMF/acetone and obtained as a white powder.

The structure and purity of polymers **10**–**13** were demonstrated by ^1H and ^{13}C NMR spectroscopy and elemental analysis. A feature of particular interest was present in the ^{13}C NMR spectrum of polymer **11**, as it shows a complex pattern in the aliphatic carbon atom region (Figure 1).

Four distinct resonances are evident in the spectrum for the methoxy carbon atom (signal **b**) and for the α carbon atom of the ethylhexyloxy chain (signal **a**), whereas three resonances are present for the β carbon atom, which is likely to result from the overlap of two signals (signal **c**). These resonances may be due to the presence of different connection possibilities between the repeating units in the polymer chain [head-to-head (HH), head-to-tail (HT), tail-to-head (TH) and tail-to-tail (TT)] (Figure 2).

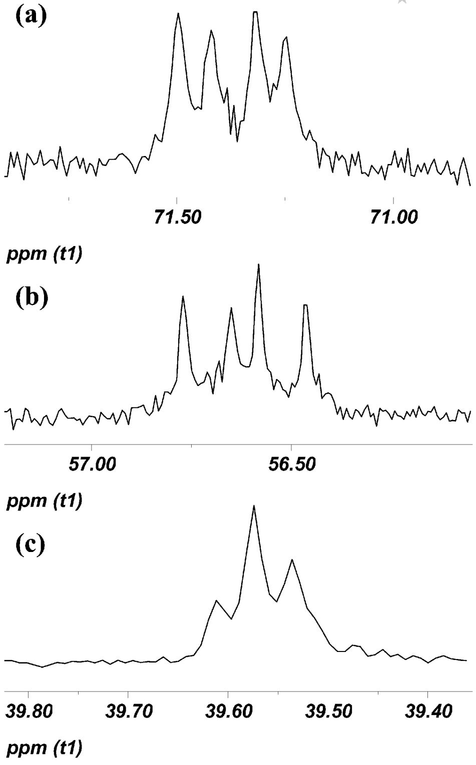


Figure 1. ^{13}C NMR spectrum of **11**: four peaks for signals **a** and **b** and three peaks for signal **c**.

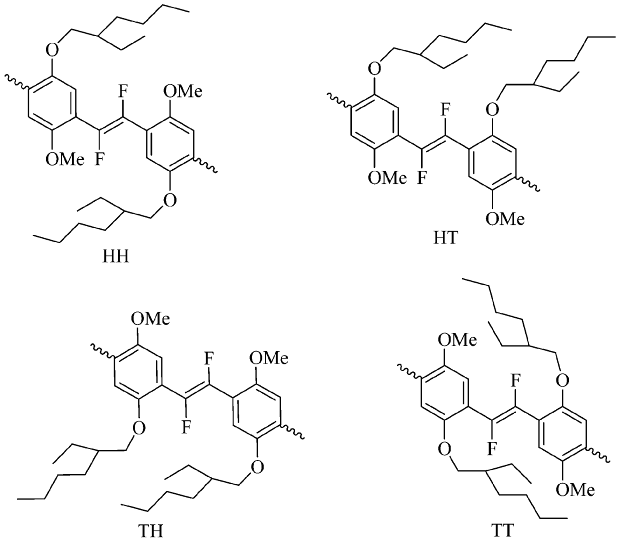


Figure 2. Expected connections in the polymer chain of **11**.

In the same way, the ^{19}F NMR spectrum shows four different peaks for the vinylic fluorine atoms. This signal splitting in the ^{13}C NMR spectrum is in agreement with that observed by Penzkofer and coworkers[19] in the spectroscopic characterization of Gilch-type and Horner-type MEH-PPV.

Yields, weights (M_w) and numerals (M_n), average molecular weights and polydispersivities (M_w/M_n) of polymers **10**–**13** are summarized in Table 1.

Table 1. Summary of yields, molecular weights and polydispersivities of polymers **10**–**13**.

Polymer	Yield [%]	M_w[a]	M_w/M_n	M_n[a]
10	55	65150[b]	1.6	40720[b]
11	87	47000	1.7	27820
12	82	45600	2.0	23000
13	50	47100	2.9	16500

[a] Determined by conventional size exclusion chromatography (SEC), polystyrene narrow standards calibration and THF as mobile phase. [b] Determined with a multiangle light-scattering (MALS) detector on-line to a SEC system and *N*,*N*-dimethylacetamide (DMAc) + lithium chloride (0.1 M) as mobile phase.

The first notable feature upon examination of these data (Table 1) is the relatively high molecular weight of polymers **10**–**13**; this is unusual for polymers obtained from Stille cross-coupling reactions. Indeed, the reaction of 1,2-bis(tributylstannyl)ethene with aryl dihalides generally affords relatively low molecular weight arylenevinylene polymers.[9] The rather high degree of polymerization obtained with difluorostannyl derivative **4** may be ascribed to an apparent higher reactivity of **4** with respect to that of its nonfluorinated counterpart. This observation, however, warrants deeper investigation, as the transmetallation process in the catalytic cycle of the Stille cross-coupling reaction, which is generally considered the rate-determining step, should be hampered by the presence of strong electron-withdrawing groups on the organometallic reagent.

A second relevant result is represented by the strong hypsochromic shift of the spectral properties induced by the presence of the fluorine atoms on the vinylene units, which results in blue-light emission from polymers **10**–**12** (Table 2). Moreover, the absorption and emission spectra of PPV polymers **10** and **11** appear to be markedly blueshifted in comparison with those of PPDFV (λ_{max}^{abs} = 390 nm, λ_{max}^{em} = 580 nm) and DMOS-PPDFV (λ_{max}^{abs} = 385 nm, λ_{max}^{em} = 485 nm), which are the only other reported PPVs with fluorinated vinylene units.[6] To the best of our knowledge, polymer **11** shows the most blueshifted photoluminescence emission in the solid state reported to date for poly(*p*-phenylenevinylene)s.[20] Further photophysical and theoretical investigations are in progress in order to ascertain the role of the fluorine atoms in the emission properties of these materials and in the supramolecular organization in their solid state.

Table 2. Summary of absorption maxima, emission maxima and absolute photoluminescence quantum yields (PL) in solution and thin films of polymers **10**–**13**.

Polymer	λ_{max}^{Abs} (sol.)[a]	λ_{max}^{Em} (sol.)[a]	λ_{max}^{Em} (film)	PL$^{sol.}$ [%][a]	PL^{film} [%]
10	352[b]	460, 383[b]	497, 462	1.4[b]	1.0
11	360	468	458	4.7	10.0
12	435, 412	481, 450	487, 457	75	5.0
13	394	534	598	0.3	0.2

[a] Measured in chloroform. [b] Measured in DMSO.

Conclusions

Our investigation has furnished a general and straightforward synthetic approach to poly(arylenevinylene) polymers with fluorinated double bonds. Interestingly, the molecular weights of the polymers obtained are much higher than those expected by using an organometallic route (Stille cross-coupling reaction) for polymerization. The optical characterization of the polymers reported indicates that the introduction of the fluorine atoms on the double bonds as a structural modification is useful for blueshifting spectral characteristics. In particular, polymer **11**, a fluorinated counterpart of the well-known MEH-PPV, has the most blueshifted emission of all PPVs reported to date.

Experimental Section

All reagents were obtained from commercial sources. Toluene, tetrahydrofuran (THF) and diethyl ether were freshly distilled from sodium and benzophenone under a nitrogen atmosphere immediately prior to use. Dimethylformamide (DMF) was distilled from 4 Å molecular sieves. FTIR spectra were measured with a Perkin–Elmer 1710 spectrophotometer by using dry KBr pellets. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or [D$_6$]DMSO with a Bruker AM 500 spectrometer at 500 and 125 MHz, respectively. ^{19}F NMR spectra were recorded in $CDCl_3$ or [D$_6$]DMSO with a Varian Inova 400 spectrometer at 376 MHz. The residual $CHCl_3$ (or DMSO) signal at δ = 7.24 (or 2.49) ppm and the $CDCl_3$ (or [D$_6$]DMSO) signal at δ = 77.0 (or 39.5) ppm were used as standards for ^{1}H and ^{13}C NMR spectra, respectively. $CFCl_3$ was used as an internal standard for ^{19}F NMR spectra. MS spectra were recorded with a Shimadzu GCMS-QP 5000 spectrometer. UV/Vis spectra were recorded with a Shimadzu UV-2401 PC spectrophotometer. Emission spectra were recorded with a Varian Cary Eclipse Fluorimeter. Molecular weights were determined by SEC with a Hewlett–Packard HP 1050 liquid chromatograph instrument equipped with a Plgel 5 µ Mixed-D300 × 7.5 mm column. The multiangle light scattering (MALS) detector was a Dawn DSP-F photometer from Wyatt. Elemental analyses were performed with a Carlo Erba CHNS-O EA1108-Elemental Analyzer. A Büchi GKR-51 apparatus was used to purify the liquid products by distillation. The measurements of the absolute value of photoluminescence (PL) quantum efficiency (QY), both in solution and in thin films, were performed with a Fluorolog Horiba Jobin Yvon spectrofluorimeter equipped with an integrating sphere with a reflectivity >99% in the Vis/NIR range, The PLQY was determined relative to the depletion of the excitation intensity (i.e. the absorption), following the procedure described in literature.[21]

All optical investigations were carried out at room temperature with thin films (70–120 nm) of polymer prepared by spin coating from a chloroform solution (DMSO solution for polymer **10**; approximately 2 wt.-%, filtered with 5 µm syringe filters). Quartz substrate was used for the PL experiments in the solid state and a KLA Tencor ALPHA-STEP 500 surface profiler was used to determine the thin thicknesses.

1,1,2-Trifluorotriethylsilylethene (1): A three-neck, 500-mL round-bottomed flask equipped with a dry ice/2-propanol-cooled cold finger condenser and nitrogen tee was charged with chlorotriethylsilane (25.0 g, 165.9 mmol) and dry THF (115 mL). The solution was stirred and cooled to –90 °C. Chlorotrifluoroethene (17.8 g, 199.0 mmol) was then condensed into the flask by the cold finger condenser. Butyllithium (2.5 M in hexanes, 68 mL, 170 mmol) was added dropwise to the solution over 2 h whilst the temperature was maintained below –90 °C. The reaction mixture was stirred at –90 °C for 4 h and then warmed to room temperature overnight. The reaction mixture was quenched slowly with a saturated aqueous solution of NH_4Cl (70 mL). The organic layer was washed with water (70 mL), dried with anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by distillation with a Vigreux column to yield a colourless liquid product (28.65 g, 88%). B.p. 144 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 0.99 (t, J = 7.9 Hz, 9 H), 0.73 (q, J = 7.9 Hz, 6 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 161.97 (ddd, $^{1}J_{\mathrm{C,F}}$ = 276 Hz, $^{1}J_{\mathrm{C,F}}$ = 310 Hz, $^{2}J_{\mathrm{C,F}}$ = 40 Hz), 130.51 (ddd, $^{1}J_{\mathrm{C,F}}$ = 256 Hz, $^{2}J_{\mathrm{C,F}}$ = 69 Hz, $^{2}J_{\mathrm{C,F}}$ = 2.8 Hz), 6.82, 2.00 ppm. GC–MS (EI, 70 eV): *m*/*z* (%) = 196 (3) $[M]^+$, 167 (21).

(*Z*)-1,2-Difluorotriethylsilylethene (2): A three-necked, 500-mL, round-bottomed flask equipped with a dropping funnel, thermometer and nitrogen tee was charged with 1,1,2-trifluorotriethylsilylethene (**1**, 28.0 g, 142.6 mmol) and dry THF (40 mL). The solution was stirred and cooled to –10 °C. Lithium aluminium hydride (1 M in THF, 150 mL, 150 mmol) was added dropwise over 1 h whilst the internal temperature of the reaction mixture was maintained below 0 °C. The reaction mixture was stirred at room temperature for 4 h and then quenched cautiously by its slow addition to ice/water. The organic layer was diluted with diethyl ether (200 mL), washed with HCl (2 N, 200 mL) and saturated aqueous $NaHCO_3$ (100 mL), dried with anhydrous Na_2SO_4 and concentrated under reduced pressure. The remaining residue was purified by distillation with a Vigreux column to yield a colourless liquid product (25.4 g, 87%). B.p. 145 °C. *Z*/*E*, 95:5. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.62 (dd, $^{2}J_{\mathrm{H,F}}$ = 80 Hz, $^{3}J_{\mathrm{H,F\,=}}$ 11 Hz, 1 H), 1.00 (t, J = 8.0 Hz, 9 H), 0.75 (q, J = 8.0 Hz, 6 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 160.78 (dd, $^{1}J_{\mathrm{C,F}}$ = 260 Hz, $^{2}J_{\mathrm{C,F}}$ = 58 Hz), 154.35 (dd, $^{1}J_{\mathrm{C,F}}$ = 240 Hz, $^{2}J_{\mathrm{C,F}}$ = 58 Hz), 6.86, 2.10 ppm. GC–MS (EI, 70 eV): *m*/*z* (%) = 178 (2) $[M]^+$, 149 (5), 121 (21), 105 (97), 77 (100).

(*Z*)-1,2-Difluoroethenyltributylstannane (3): A three-necked, 500-mL, round-bottomed flask equipped with a cold water condenser and nitrogen tee was charged with (*Z*)-1,2-difluorotriethylsilylethene (**2**, 25.0 g, 140 mmol), anhydrous potassium fluoride (11.4 g, 196 mmol) and dry DMF (100 mL). Tributyltin chloride (45.6 g, 140 mmol) was added, and the reaction mixture was stirred at 70 °C overnight. The reaction mixture was extracted with hexane and washed several times with water. The organic layer was dried with anhydrous Na_2SO_4, and the solvent was distilled under reduced pressure to yield a crude light-yellow liquid. The final product was isolated as a colourless liquid (49.4 g, 80%) by distillation with a Kugelrohr apparatus (4 mbar, 75 °C). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.69 (dd, $^{2}J_{\mathrm{H,F}}$ = 83 Hz, $^{3}J_{\mathrm{H,F}}$ = 11 Hz, 1 H), 1.55 (quint, J = 8.0 Hz, 6 H), 1.33 (sext, J = 8.0 Hz, 6 H), 1.09 (t, J = 8.0 Hz, 6 H), 0.90 (t, J = 8.0 Hz, 9 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.81 (dd, $^{1}J_{\mathrm{C,F}}$ = 298 Hz, $^{2}J_{\mathrm{C,F}}$ = 79 Hz), 153.76 (dd, $^{1}J_{\mathrm{C,F}}$ = 230 Hz, $^{2}J_{\mathrm{C,F}}$ = 48 Hz), 28.76, 27.09, 13.61, 9.78 ppm. GC–MS (EI, 70 eV): *m*/*z* (%) = 297 (18) $[M - C_4H_9]^+$, 241 (43), 183 (17).

(*E*)-(1,2-Difluoro-1,2-ethenediyl)bis(tributylstannane) (4): A three-necked, 500-mL, round-bottomed flask equipped with two dropping funnels and nitrogen tee was charged with dry THF (300 mL) and 2,2,6,6-tetramethylpiperidine (9.6 g, 68 mmol). The reaction solution was cooled to –20 °C and butyllithium (29.5 mL, 73.6 mmol) was added dropwise. The reaction mixture was stirred at –5 to –10 °C for another 30 min, cooled to –90 °C and (*Z*)-1,2-difluoroethenyltributylstannane (**3**, 20.0 g, 56.6 mmol) was added dropwise. After the addition and stirring at –90 °C for 2 h, tributyltin chloride (19.4 g, 59.6 mmol) was added dropwise. The reaction mixture was stirred at –90 °C for 2 h and warmed to room temperature overnight. After extracting with diethyl ether (500 mL) and washing with saturated aqueous KF (2 × 100 mL) and water (2 × 500 mL), the organic layer was separated and dried with anhydrous Na_2SO_4, filtered and then the solvent was removed under reduced pressure. The residue was distilled by Kugelrohr apparatus (2×10^{-4} mbar, 150 °C) to yield the pure product as colourless liquid (34.5 g, 95%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.56 (quint, J = 8.0 Hz, 12 H), 1.34 (sext, J = 8.0 Hz, 12 H), 1.07 (t, J = 8.0 Hz, 12 H), 0.91 (t, J = 8.0 Hz, 18 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ = 174.43 (dd, $^{1}J_{\mathrm{C,F}}$ = 313 Hz, $^{2}J_{\mathrm{C,F}}$ = 100 Hz), 28.92, 27.12, 13.64, 10.00 ppm. GC–MS (EI, 70 eV): *m*/*z* (%) = 585 (15) $[M - C_4H_9]^+$, 291 (45), 235 (71).

Sodium 3-(4-Methoxyphenoxy)propane-1-sulfonate (5): A three-necked, 100-mL, round-bottomed flask was charged with 4-methoxyphenol (2.5 g, 20.1 mmol), dry toluene (20 mL) and sodium hydride NaH (60% dispersion in mineral oil, 0.48 g, 20.1 mmol) under a nitrogen atmosphere. The reaction mixture was stirred for 30 min and then 1,3-propanesultone (3.0 g, 20.1 mmol) was added in one portion. The reaction mixture was heated at reflux overnight and then cooled to room temperature. The obtained precipitate was filtered. The solid was recrystallized twice from DMF/acetone to yield the product as a white powder (4.4 g, 82%). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 6.84 (s, 4 H), 3.97 (t, J = 6.5 Hz, 2 H), 3.68 (s, 3 H), 2.58 (t, J = 7.5 Hz, 2 H), 1.98 (quint, J = 7.0 Hz, 2 H) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 153.18, 152.56, 115.28, 114.52, 67.00, 55.29, 47.91, 25.24 ppm. FTIR (KBr): $\tilde{\nu}$ = 1512, 1242, 1216, 1190, 1173, 1063, 1037, 828 cm^{-1}. $C_{10}H_{13}NaO_5S$ (268.26): calcd. C 44.77, H 4.88, S 11.95; found C 44.57, H 5.10, S 11.80.

Sodium 3-(2,5-Diiodo-4-methoxyphenoxy)propane-1-sulfonate (6): A 100-mL, round-bottomed flask was charged with **5** (2 g, 7.46 mmol), I_2 (1.7 g, 6.70 mmol), HIO_3 (0.8 g, 4.55 mmol), H_2SO_4 (30% aqueous solution, 3 mL), CCl_4 (3 mL) and acetic acid (12 mL). The resulting mixture was heated at 75 °C overnight. The reaction mixture was cooled to room temperature, and the obtained precipitate was filtered. The solid was recrystallized twice from DMF/acetone to yield product **6** as a white powder (3.26 g, 84%). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 7.32 (s, 1 H), 7. 31 (s, 1 H), 4.04 (t, J = 6.3 Hz, 2 H), 3.77 (s, 3 H), 2.58 (t, J = 6.3 Hz, 2 H), 1.97 (quint, J = 6.3, Hz, 2 H) ppm. ^{13}C NMR (125 MHz, [D$_6$]-DMSO): δ = 152.80, 152.17, 122.44, 121.13, 86.91, 86.03, 68.82, 57.00, 47.95, 25.24 ppm. FTIR (KBr): $\tilde{\nu}$ = 1485, 1350, 1210, 1061 cm^{-1}. $C_{10}H_{11}I_2NaO_5S$ (520.05): calcd. C 23.10, H 2.13, S 6.17; found C 23.02, H 2.4, S 6.0.

Typical Polymerization Reaction – Synthesis of Poly(2-methoxy-5-[(2-ethylhexyl)oxy]-1,4-phenylenedifluorovinylene) (MEH-PPDFV, 11): A mixture of 2,5-diiodo-4-[(2-ethylhexyl)oxy]methoxybenzene (**5**, 3.80 g, 7.78 mmol), (*E*)-(1,2-difluoro-1,2-ethenediyl)bis(tributylstannane) (**4**, 5.0 g, 7.78 mmol), tetrakis(triphenylphosphane)palladium(0) (0.45 g, 0.39 mmol) and cuprous iodide (1.48 g, 7.78 mmol) in dry THF (50 mL) and dry DMF (50 mL) was stirred at room temperature under a nitrogen atmosphere. The reaction mixture quickly turned dark in colour and after 2 d it changed to a dark-green solution. After 6 d the polymer was capped by adding phenyltributyltin (2.65 g, 7.78 mmol), and the solution was stirred for 1 d. Iodobenzene (159 g, 7.78 mmol) was then added and stirring was continued for another day. The reaction mixture was quenched with water and extracted with dichloromethane (3 × 100 mL). The combined organic layer was washed consecutively with saturated aqueous ammonium chloride (3 × 100 mL) and water (200 mL). The crude residue, obtained after evaporation of the solvent under reduced pressure, was purified by extracting in a Soxhlet apparatus sequentially with hexane (24 h) and ethanol (24 h) to remove low molecular weight materials and then with chloroform to recover the polymer. After evaporation of the solvent under reduced pressure, the pure polymer was recovered as a green powder (2.0 g, 87%). ^{19}F NMR (376 MHz, CDCl$_3$): δ = –138.64 (s, 1 F), –138.83 (s, 1 F), –138.92 (s, 1 F), –139.35 (s, 1 F) ppm. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.1–7.2 (br. s, 2 H), 4.0–3.85 (br. s, 5 H), 1.8–1.7 (br. s, 1 H), 1.6–1.2 (br. s, 8 H), 1.0–0.8 (br. s, 6 H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = 151.13, 151.08, 146.19 (dd, $^{1}J_{C,F}$ = 299 Hz, $^{2}J_{C,F}$ = 113 Hz), 121.13, 120.94, 114.48 (dd, $^{2}J_{C,F}$ = 58 Hz, $^{3}J_{C,F}$ = 18 Hz), 71.51, 71.43, 71.32, 71.26, 56.77, 56.65, 56.58, 56.47, 39.62, 39.58, 39.54, 30.45, 29.05, 23.87, 23.03, 14.03, 11.19 ppm. FTIR (KBr): $\tilde{\nu}$ = 2957, 2929, 2872, 1507, 1462, 1408, 1215, 1124, 1035 cm^{-1}. $C_{17}H_{22}F_2O_2$ (296.36): calcd. C 68.90, H 7.48; found C 68.61, H 7.38.

Poly(2-methoxy-5-propyloxysulfonate)-1,4-phenylenedifluorovinylene (MPS-PPDFV, 10): Purified by recrystallization from DMF/acetone. Yield: 55%. ^{19}F NMR (376 MHz, CDCl$_3$): δ = –135.08 to –137.2 (br. s, 1F), –136.70 to –137.08 (br. s, 1F) ppm. ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ = 7.4–7.2 (br. s, 2 H), 4.3–4.1 (br. s, 2 H), 4.0–3.8 (br. s, 3 H), 3.0–2.5 (br. s, 2 H), 2.3–1.9 (br. s, 2 H) ppm. ^{13}C NMR (125 MHz, [D$_6$]DMSO): δ = 150.27, 149.51, 145.02 (dd, $^{1}J_{C,F}$ = 305 Hz, $^{2}J_{C,F}$ = 117 Hz), 119.79 (d, $^{2}J_{C,F}$ = 65 Hz), 114.61, 113.45, 67.78, 55.92, 49.49, 24.77 ppm. FTIR (KBr): $\tilde{\nu}$ = 1506, 1411, 1216 cm^{-1}. $C_{12}H_{11}F_2NaO_5S$ (328.26): calcd. C 43.91, H 3.38, S 9.77; found C 43.50, H 2.95, S 9.77.

Poly(9,9-dihexyl)-2,7-fluorenylenedifluorovinylene (PDHFDFV, 12): Purified according to the procedure used for polymer **11** and obtained as a light-green powder. Yield: 82%. ^{19}F NMR (376 MHz, CDCl$_3$): δ = –150.18 (s, 2 F) ppm. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 8.0–7.7 (br. s, 6 H), 2.2–1.9 (br. s, 4 H), 1.2–0.95 (br. s, 12 H), 0.85–0.6 (br. s, 10 H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = 151.40, 148.94 (dd, $^{1}J_{C,F}$ = 280 Hz, $^{2}J_{C,F}$ = 92 Hz), 141.17, 129.57, 124.92, 120.13, 55.52, 40.36, 31.50, 29.68, 23.76, 22.59, 13.98 ppm. FTIR (KBr): $\tilde{\nu}$ = 2927, 2856, 1473, 1248, 1125, 892, 822 cm^{-1}. $C_{27}H_{32}F_2$ (394.55): calcd. C 82.19, H 8.17; found C 82.38, H 8.13.

Poly(3,4-dibutyl)-2,5-thienylenedifluorovinylene (PDBTDFV) (13): Purified by extraction with dichloromethane and precipitated by adding methanol and then recrystallized from CH_2Cl_2/MeOH. Yield: 50%. ^{19}F NMR (376 MHz, CDCl$_3$): δ = –135.56 (s, 2 F) ppm. ^{1}H NMR (500 MHz, CDCl$_3$): δ = 2.8–2.6 (br. s, 4 H), 1.7–1.2 (br. s, 8 H), 1.0–0.8 (br. s, 6 H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ = 144.24 (dd, $^{1}J_{C,F}$ = 295 Hz, $^{2}J_{C,F}$ = 106 Hz), 144.03 (dd, $^{2}J_{C,F}$ = 46 Hz, $^{3}J_{C,F}$ = 9 Hz), 134.88, 126.20, 31.17, 28.04, 22.98, 13.86 ppm. FTIR (KBr): $\tilde{\nu}$ = 2958, 2930, 2872, 1463, 1378, 1280, 1116 cm^{-1}. $C_{14}H_{18}F_2S$ (256.35): calcd. C 65.60, H 7.08, S 12.51; found C 65.72, H 6.88, S 12.77.

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