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Poly(arylene vinylene) Synthesis via a Precursor Step-growth Polymerization Route Involving the Ramberg-Bäcklund Reaction as a Key Post-chemical Modification Step

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ABSTRACT: The synthesis of conjugated copolymers based on poly(fluorene vinylene) [PFV] and poly(fluorene vinylene-*co*-carbazole vinylene) [PFVCV] was achieved *via* a previously unexplored precursor three-step synthetic route involving the Ramberg-Bäcklund reaction. The resulting π -conjugated (co)polymers proved highly soluble in common organic solvents, such as DCM, THF, or CHCl₃. The solution step-growth polymerization between 2,7-bis(bromomethyl)-9,9'-dihexyl-9*H*-fluorene [F-Br] and 2,7-bis(mercaptomethyl)-9,9'-dihexyl-9*H*-fluorene [F-SH] was carried out under basic conditions at 100 °C in a mixture of MeOH and THF. The resulting polysulfides were then subjected to an oxidation reaction using *m*-CPBA, which was followed by the Ramberg-Bäcklund reaction in the presence of CF₂Br₂/Al₂O₃-KOH, thus achieving the desired PFV. Similarly, PFVCV could be synthesized through the same three-step sequence employing, in this case, 2,7-bis(mercaptomethyl)-9-(tridecan-7-yl)-9*H*-carbazole (C-SH) and F-Br. Conjugated polymers with apparent molecular weights up to 15 kg.mol⁻¹ and exhibiting promising optical features were obtained following this convenient synthetic strategy.

INTRODUCTION

In recent years, thin-film device technologies employing π -conjugated polymers have attracted a great deal of attention owing to their properties suitable for electronic and optoelectronic applications, including organic transistors,¹⁻² bulk heterojunction solar cells for organic photovoltaics (OPV)³⁻⁴ or organic light emitting diodes (OLED).⁵ The solution-processability of π -conjugated polymers, combined with their optoelectronic properties, such as light absorption, carrier mobility and exciton dynamics, can be fine-tuned through subtle changes in their structure. Molecular parameters include molecular weight, bond length alternation, substituent effects, aromaticity, planarity, regioregularity, intermolecular interactions, etc. Hence, simple synthetic modifications can dramatically impact optoelectronic and thin film self-assembled properties. Most π -conjugated polymers consist of sp^2 -hybridized carbon atoms and are based on aryl-aryl or aryl-vinyl repeating units, mostly through alternation between C-C and C=C bonds.⁶ Heteroatoms can be introduced in the π -conjugation system: for instance, the $-C=N-$ double bond is somehow electrically equivalent to the $-C=C-$ one.

In this context, poly(*p*-phenylene vinylene)- (PPV)-type π -conjugated polymers represent a special class of highly fluorescent, highly stable polymeric semiconductors.⁷⁻⁸ PPV-like materials can be synthesized by a wide variety of synthetic routes, either following a step-growth or a chain-growth polymerization pathway. Step-growth polymerization methods directly leads to PPV oligomers and rely on well-established elementary reactions of molecular chemistry, such as the Knoevenagel condensation,⁸ the Wittig or Horner-Wadsworth-Emmons olefination,^{9,10,11} the palladium-catalyzed Stille, Suzuki or Heck coupling¹² and the Siegrist reaction.¹³ Alternatively, chain-growth polymerization methods allow achieving higher molecular weights. However, the final PPV material is often obtained by post-chemical modification of a polymer precursor as for instance in Gilch,¹⁴ Wessling sulfonium,¹⁵⁻¹⁶ dithiocarbamate (or xanthate), and sulfinyl routes.¹⁷⁻¹⁸ In order to alleviate solubility issues and facilitate their processability, specific groups can be introduced in 2- and 5-positions of the aromatic ring of PPV-type materials. Controlled living polymerization has also been considered for PPV synthesis.¹⁹ With the exception of PPV's grown both by the latter method under specific conditions and by ring-opening metathesis polymerization (ROMP), relatively poor control over molecular weights and dispersities generally characterize these polymerization routes. More generally, these synthetic methods to PPV's, although straightforward, still show some limitations, including: (a) structural defects due to incomplete post-chemical modification by thermal conversion or oxidation (b) modest molecular weights (c) generation of toxic side products during the elimination process (d) gelation or precipitation of the polymeric products, which may occur during polymerization (e) limited control over the *E/Z* content of the vinyl bridge (f) use of costly and non-renewable metal catalysts and, last but not least, (g) the presence of residual metallic traces, which require lengthy and tedious purification steps.²⁰

On this basis, we envisioned developing novel PPV-like materials following a previously unexplored precursor step-growth polymerization route/post-chemical functionalization sequence, involving a three-step sequence of reactions (Figure 1). The first step (i) is achieved by step-growth polymerization in solution of dibromides and dithiols as monomers, forming polysulfides. The second step (ii) consists in oxidizing these polymer precursors into polysulfones, which is followed by an ultimate step (iii) of elimination, *via* the so-called Ramberg-Bäcklund reaction.²¹ The Ramberg-Bäcklund reaction is very versatile for the construction of carbon-carbon double bonds, and has been largely applied in the context

of total synthesis of complex natural products. Only recent reports have described its application in dendrimer synthesis.²² This reaction involves a suitably designed sulfone precursor, which upon α -halogenation under basic conditions, provides the corresponding olefin generally in high yields. It is thus a simple way to create C=C double bonds under mild conditions, starting from readily available substrates. Another advantage of this process is that it allows the coupling around the sulfonyl group of identical or differentiated substituents, on purpose, in a limited number of steps. Starting materials are easily available and provide olefins without alkene rearrangements under mild alkaline conditions. *E/Z*-stereocontrol mainly relies on the nature of the base, with mild bases favoring the *Z*-isomer, while *E*- is generally formed in the presence of stronger bases. Many examples have demonstrated that the Ramberg-Bäcklund process can be applied to the preparation of polysubstituted alkenes, including tetrasubstituted ones as well as polyenes.²¹ Iterative synthesis of oligo-PPV's has been described,²³⁻²⁴ but to the best of our knowledge, this reaction has never been applied to the synthesis of polyolefins starting from polysulfones. The synthetic approach we devise here opens a general and straightforward access to symmetrical PPV-like materials bearing identical aromatic fragments (**Route A**, Figure 1). By varying the nature of aryl groups, the optoelectronic properties could be tuned depending on the targeted application (OPV, OLED ...).²⁵⁻²⁶ Furthermore, the conjunctive nature of the Ramberg-Bäcklund process should be particularly appealing for the design of alternating monomer units along the π -conjugated backbone (**Route B**, Figure 1). For example, it could allow the formation of “donor-acceptor” alternating low band gap copolymers, by using electron-rich and electron-poor monomer units. Such copolymers are characterized by an extended optical absorption to the red region, and allow for a better manipulation of the HOMO/LUMO levels, providing conjugated systems with relatively high charge carrier mobility.²⁷⁻³¹

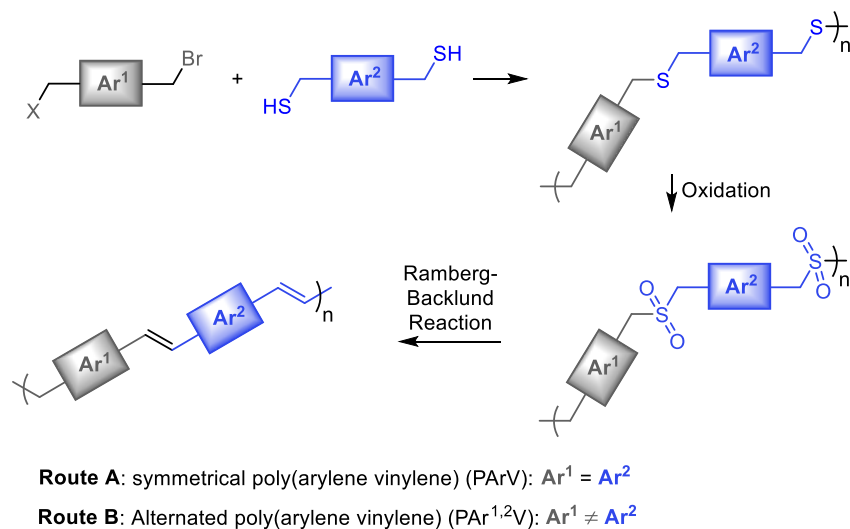


Figure 1. Synthetic strategies toward poly(arylene vinylene)s (PPV's) based on the Ramberg-Bäcklund reaction.

As an example of the potentiality of these arylene-vinylene polymers, recently, Nomura and coll. have obtained PPV's with different end-groups by combining acyclic diene metathesis polymerization with Wittig-type couplings.^{32,33} Here we describe the synthetic developments validating both strategies, by reporting the synthesis of poly(fluorene vinylene)- and poly(fluorene-carbazole vinylene)-type conjugated (co)polymers.

EXPERIMENTAL SECTION

All reactions were carried out under an argon atmosphere with solvents dried over activated alumina columns on MBraun Solvent Purification System (SPS-800), unless otherwise noted.

All reagent-grade chemicals were obtained from commercial suppliers and were used as received, unless otherwise stated. ^1H NMR and ^{13}C NMR were recorded on various spectrometers: a Bruker Avance 300 (^1H : 300 MHz, ^{13}C : 75.46 MHz), a Bruker Avance 400 (^1H : 400 MHz, ^{13}C : 100.6 MHz) using CDCl_3 as internal reference unless otherwise indicated. The chemical shifts (δ) and coupling constants (J) are expressed in ppm and Hz respectively. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. FT-IR spectra were recorded on a Perkin-Elmer Spectrum 100 using a diamond ATR accessory. High-resolution mass spectra (HRMS) were recorded with a Waters QTOF 2 spectrometer in the electrospray ionization (ESI) mode. Melting points were not corrected and determined by using a Stuart Scientific SMP3 apparatus. Analytical thin layer chromatography was performed using silica gel 60 F254 pre-coated plates (Merck) with visualization by ultraviolet light, potassium permanganate. Flash chromatography was performed on silica gel (0.043-0.063 mm) with ethyl acetate (EtOAc) and petroleum ether (PE) as eluents unless otherwise indicated.

2,7-Bis(hydroxymethyl)-9,9'-dihexyl-9H-fluorene (2). To a stirred solution of 9,9'-dihexyl-9H-fluorene-2,7-dicarbaldehyde **1**³⁴ (4.29 g, 11 mmol) in a 3:1 THF/MeOH mixture (100 mL), NaBH_4 (3.34 g, 88 mmol) was added portion wise at 0°C and then the reaction mixture was allowed to warm to room temperature for 4 h. The reaction was quenched with aq. NH_4Cl solution (10 mL), and the aqueous layer extracted with ethyl acetate (2 x 50 mL). The organic layer was then dried over anhydrous Na_2SO_4 and solvents evaporated to give a crude mixture which was purified by flash column chromatography (silica, EtOAc/PET 1:9), affording the desired compound as a white solid (3.46 g, 80%). The spectral data are consistent with those reported in the literature.³⁵

Mp = $74\text{--}76^\circ\text{C}$; IR (ATR) ν_{max} (cm^{-1}): 3285, 2925, 2854, 1457; ^1H NMR (300 MHz, CDCl_3): δ 0.52-0.68 (m, 4H), 0.70-0.82 (m, 6H), 0.94-1.18 (m, 12H), 1.88 (br, 2H), 1.90-2.02 (m, 4H), 4.75 (s, 4H), 7.27-7.36 (m, 4H), 7.62-7.70 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 13.97, 22.56, 23.71, 29.67, 31.47, 40.32, 54.99, 65.72, 119.64, 121.49, 125.73, 139.74, 140.35, 151.30; HRMS: Calcd. for $\text{C}_{27}\text{H}_{38}\text{O}_2$ $[\text{M}]^+$ 394.28718, found 394.28862.

2,7-Bis(bromomethyl)-9,9'-dihexyl-9H-fluorene (F-Br). To a stirred solution of **2** (1.54 g, 3.91 mmol) in benzene (20 mL), PBr_3 (1.09 mL, 11.7 mmol) was slowly added at room temperature, then the reaction mixture was heated to 45°C for 6 h. The reaction was quenched with water (10 mL) and extracted with dichloromethane (2 x 25 mL). The organic layer was dried over anhydrous Na_2SO_4 and solvents evaporated to give a crude mixture which was purified by flash column chromatography (silica, CH_2Cl_2 /PET 1:9) to afford the compound **F-Br** as a white solid (1.21 g, 59%). The spectral data are consistent with literature data.³⁵

Mp = $51\text{--}53^\circ\text{C}$; IR (ATR) ν_{max} (cm^{-1}): 2924, 1468, 1291; ^1H NMR (300 MHz, CDCl_3): δ 0.53-0.68 (m, 4H), 0.70-0.82 (m, 6H), 0.95-1.18 (m, 12H), 1.90-2.02 (m, 4H), 4.59 (s, 4H), 7.32-7.39 (m, 4H), 7.59-7.68 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3): δ 13.98, 22.46, 23.61, 29.51, 31.34, 34.43, 40.05, 55.11, 120.03, 123.64, 127.98, 136.86, 140.71, 151.63; HRMS: Calcd. for $\text{C}_{27}\text{H}_{36}\text{Br}_2$ $[\text{M}]^+$ 518.11838, found 518.12470.

2,7-Bis(mercaptomethyl)-9,9'-dihexyl-9H-fluorene (F-SH). Following a slightly modified literature procedure,³⁶ to a stirred solution of **F-Br** (1.04 g, 2 mmol) in EtOH (10 mL), thiourea (0.334 g, 4.40 mmol) was added and the reaction mixture was heated to reflux for 4 h. Then, the solvent was evaporated under vacuum, the solid obtained was hydrolyzed with 50% aqueous sodium hydroxide solution (10 mL) and extracted with EtOAc (2 x 25 mL). The organic layer was dried over anhydrous Na₂SO₄, and solvents evaporated to give a crude mixture, which was purified by flash column chromatography (silica, CH₂Cl₂/PET 3:7) to afford the desired compound **F-SH** as a white solid (0.42 g, 49%).

mp: 39-41°C; IR (ATR) ν_{\max} (cm⁻¹): 2925, 2556, 1520; ¹H NMR (300 MHz, CDCl₃): δ 0.54-0.68 (m, 4H), 0.76 (t, 6H, *J* = 6.9 Hz), 0.95-1.18 (m, 12H), 1.77 (t, 2H, *J* = 7.5 Hz), 1.86-1.98 (m, 4H), 3.82 (d, 4H, *J* = 7.5 Hz), 7.22-7.30 (m, 4H), 7.54-7.62 (m, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 13.98, 22.49, 23.64, 29.37, 29.57, 31.37, 40.15, 54.95, 119.63, 122.48, 126.69, 139.69, 139.91, 151.34; HRMS: Calcd. for C₂₇H₃₈S₂ [M]⁺: 426.24149, found 426.24213.

Synthesis of PF-S. In a sealed tube, a solution of **F-Br** (1.04 g, 2 mmol) and **F-SH** (0.85 g, 2 mmol) in a 1:1 THF/MeOH mixture (20 mL) was treated with powdered KOH (0.34 g, 6 mmol) and the reaction mixture was heated to 100 °C for 14 h. Then, the reaction mixture was cooled to room temperature and the solvent evaporated under vacuum. The crude reaction mixture was washed with H₂O (20 mL), MeOH (20 mL) and the solid filtered. The latter was then dissolved in CHCl₃ (5 mL) and purified by precipitation using MeOH (100 mL), to provide the desired compound (**PF-S**) as a pale yellow solid (1.27 g, 78%).

IR (ATR) ν_{\max} (cm⁻¹): 2923, 2852, 1465, 817, 748; ¹H NMR (300 MHz, CDCl₃): δ 0.52-0.83 (m, 10H), 0.90-1.21 (m, 12H), 1.88-2.12 (m, 4H), 3.68 (s, 4H), 7.19-7.35 (m, 4H), 7.56-7.70 (m, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 13.98, 22.52, 23.82, 29.74, 31.56, 35.50, 40.54, 54.96, 119.56, 123.42, 127.89, 136.84, 139.87, 150.97; λ_{\max} : 290, 316 nm.

Synthesis of PF-SO. A stirred solution of **PF-S** (0.98 g, 2.5 mmol) in CHCl₃ (50 mL) was treated with *m*-CPBA (2.16 g, 12.5 mmol) and the reaction mixture was stirred at room temperature for 8 h. Then the reaction mixture was filtered and washed with CHCl₃. The filtrate was washed with saturated aqueous NaHCO₃ (2 x 25 mL), brine and water respectively. The organic solvent was evaporated and the crude compound thus obtained was purified by precipitation in a large excess of cold MeOH from a CHCl₃ solution, to afford the desired polymer as a brown solid (0.67 g, 63%).

IR (ATR) ν_{\max} (cm⁻¹): 2924, 2853, 1467, 1316, 1150, 612; ¹H NMR (300 MHz, CDCl₃): δ 0.57-0.77 (m, 10H), 0.95-1.15 (m, 12H), 1.96-2.13 (m, 4H), 4.20 (s, 4H), 7.35 (d, 2H, *J* = 7.8 Hz), 7.44 (s, 2H), 7.76 (d, 2H, *J* = 7.8 Hz); ¹³C NMR (75 MHz, CDCl₃): δ 13.93, 22.46, 23.91, 29.62, 31.50, 40.24, 55.40, 58.18, 120.43, 125.37, 126.70, 129.89, 141.15, 151.67; λ_{\max} : 290, 316 nm.

PF-SO via the rongalite[®] route. A mixture of **F-Br** (0.26 g, 0.5 mmol), rongalite[®] (0.3 g, 2.5 mmol), K₂CO₃ (0.34 g, 2.5 mmol) and tetra-*n*-butylammonium bromide (TBAB) (0.08 g, 0.25 mmol) in DMF (2.5 mL) was stirred at room temperature for 3 days. Water (5 mL) was then added to the reaction mixture. The resulting solid was filtered and washed with water (10 mL) and MeOH (10 mL). The crude compound thus obtained was purified by precipitation in a large excess of cold MeOH from a CHCl₃ solution, to obtain the **PF-SO** (0.078 g, 37%) as a white solid. The spectral data (¹H NMR) are consistent with the earlier data.

Synthesis of PFV. In a sealed round bottom flask, a stirred solution of **PF-SO** (0.20 g, 0.47 mmol) in a 1:1 THF/*t*-BuOH mixture (10 mL) was treated with freshly prepared Al₂O₃-KOH (1 g) at 0 °C and then

CF₂Br₂ (1 mL) was added at the same temperature. The reaction mixture was then stirred at room temperature for 24 h. The reaction mixture was filtered through celite and washed with CH₂Cl₂. The solvent was evaporated and the crude compound thus obtained was purified by precipitation in a large excess of cold MeOH from a CHCl₃ solution, to afford the desired polymer as a yellow solid (89 mg, 53%).

IR (ATR) ν_{\max} (cm⁻¹): 2924, 2853, 1466, 1048, 790; ¹H NMR (300 MHz, CDCl₃): δ 0.71-0.83 (m, 8H), 0.94-1.21 (m, 14H), 1.89-2.15 (m, 4H), 7.30 (s, 2H), 7.48-7.63 (m, 4H), 7.70 (d, 2H, $J = 7.8$ Hz); λ_{\max} : 426, 450 nm.

2,7-Diformyl-9-(tridecan-7-yl)-9H-carbazole (4). Following a slightly modified literature procedure,³⁷ a stirred solution of **3** (5.07g, 10 mmol) in THF (50 mL) was cooled to -78 °C and a 1.85 M solution of *n*-BuLi in hexanes (11.4 mL, 21 mmol) was added and stirred at this temperature for 1 h. Then DMF (2.3 mL, 30 mmol) in THF (10 mL) was added dropwise and the reaction mixture was allowed to warm to room temperature and stirred for 1 h. The reaction mixture was quenched with aq. NH₄Cl and extracted with EtOAc (2 x 50 mL). The organic layer was dried over anhydrous Na₂SO₄, and solvents evaporated to give a crude mixture, which was purified by column chromatography (silica gel, EtOAc/PET 1:9) to afford **4** as a yellow solid (3.26 g, 81%).

Mp = 88-90 °C; IR (ATR) ν_{\max} (cm⁻¹): 2917, 2850, 1676, 1227; ¹H NMR (300 MHz, CDCl₃): δ 0.76 (t, 6H, $J = 6.6$ Hz), 0.89-0.92 (m, 2H), 1.04-1.34 (m, 14H), 1.95-2.12 (m, 2H), 2.24-2.42 (m, 2H), 4.72 (septet, 1H, $J = 5.1$ Hz), 7.80 (d, 2H, $J = 7.8$ Hz), 8.03 (s, 1H), 8.16 (s, 1H), 8.23-8.37 (m, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 13.88, 22.38, 26.73, 28.90, 31.44, 33.75, 57.37, 110.48, 113.14, 121.08, 121.87, 126.40, 135.21, 143.24, 192.42; HRMS: Calcd. for C₂₇H₃₅NO₂ [M]⁺ 405.26678, found 405.26691.

2,7-Bis(mercaptomethyl)-9-(tridecan-7-yl)-9H-carbazole (C-SH). To a stirred solution of **4** (3.24 g, 8.0 mmol) in a 3:1 THF/MeOH mixture (60 mL), NaBH₄ (2.43 g, 64 mmol) was added portion wise at 0 °C and the reaction mixture was allowed to warm to room temperature for 4 h. The reaction was quenched with aqueous NH₄Cl solution (100 mL), extracted with EtOAc (2 x 100 mL) and the organic layer was dried over anhydrous Na₂SO₄. The solvent was then evaporated to afford the desired compound as a pale viscous liquid and used without further purification in the next step. To a stirred solution of the crude compound (2.96 g, 7.24 mmol) in benzene (30 mL), PBr₃ (1.0 mL, 21.8 mmol) was slowly added at room temperature, then the reaction mixture was heated to 45 °C for 6 h. The reaction was quenched with water (25 mL) and extracted with CH₂Cl₂ (2 x 50 mL). The organic layer was dried over anhydrous Na₂SO₄ and the solvent evaporated. The oily residue, 2,7-bis(bromomethyl)-9-(tridecan-7-yl)-9H-carbazole **5** was used in the next step without purification, since the compound was unstable under ambient condition. To a stirred solution of **5** (3.5 g, 6.5 mmol) in EtOH (30 mL) thiourea (1.5 g, 19.5 mmol) was added and the reaction mixture heated to reflux for 8 h. Then, the solvent was evaporated under vacuum, the solid obtained was hydrolyzed with 50% aqueous sodium hydroxide and extracted with EtOAc (2 x 50 mL). The organic layer was dried over anhydrous Na₂SO₄, and solvents evaporated to give a crude mixture, which was purified by flash column chromatography (silica, CH₂Cl₂/PET 3:7) to afford **C-SH** as a colorless liquid (1.56 g, 55%). The overall yield for the three steps is 47%.

IR (ATR) ν_{\max} (cm⁻¹): 2923, 2853, 2561, 1457, 1435; ¹H NMR (300 MHz, CDCl₃): δ 0.78 (t, 6H, $J = 6.6$ Hz), 0.91-1.31 (m, 16H), 1.84 (t, 2H, $J = 7.5$ Hz), 1.87-1.98 (m, 2H), 2.18-2.35 (m, 2H), 3.94 (d, 4H, $J = 7.5$ Hz), 4.53 (septet, 1H, $J = 5.1$ Hz), 7.16 (d, 2H, $J = 7.8$ Hz), 7.34 (s, 1H), 7.50 (s, 1H), 7.91-8.06 (m, 2H); ¹³C NMR (75 MHz, CDCl₃): δ 14.05, 22.58, 26.77, 29.09, 30.02, 31.60, 33.70, 56.35, 108.25,

110.95, 119.00, 120.21, 120.44, 121.36, 138.21, 138.68; HRMS: Calcd. for $C_{27}H_{39}NS_2 [M]^+$ 441.25239, found 441.25219.

Synthesis of PFC-S. In a sealed tube, a solution of **F-Br** (0.52 g, 1 mmol) and **C-SH** (0.44 g, 1 mmol) in a 1:1 THF/MeOH mixture (10 mL) was treated with powdered KOH (0.17 g, 3 mmol) and the reaction mixture was heated to 100 °C for 14 h. Then, the reaction mixture was cooled to room temperature and the solvent evaporated under vacuum. The crude reaction mixture was washed with H₂O and MeOH and the solid filtered. The latter was then dissolved in CHCl₃ (5 mL) and purified by precipitation using MeOH (100 mL) to provide the desired compound (**PFCS**) as a pale yellow solid (0.62 g, 83%).

IR (ATR) ν_{\max} (cm⁻¹): 2922, 2849, 2354, 1599, 1440; ¹H NMR (400 MHz, CDCl₃): δ 0.57-0.80 (m, 16H), 0.92-1.32 (m, 28H), 1.88-2.08 (m, 6H), 2.25-2.44 (m, 2H), 3.71 (s, 4H), 3.80 (s, 4H), 4.52-4.67 (m, 1H), 7.07-7.16 (m, 2H), 7.21-7.32 (m, 4H), 7.40 (s, 1H), 7.57 (s, 1H), 7.63 (d, 2H, $J = 7.8$ Hz), (t, 2H, $J = 8.7$ Hz); ¹³C NMR (100 MHz, CDCl₃): δ 13.96, 22.52, 23.82, 26.85, 29.14, 29.74, 31.54, 31.60, 33.83, 35.84, 36.24, 40.48, 54.96, 56.39, 109.11, 111.78, 119.50, 119.83, 120.08, 121.36, 122.73, 123.49, 127.89, 135.18, 135.58, 136.97, 139.13, 139.87, 142.55, 151.04; λ_{\max} : 245, 276, 317 nm.

Synthesis of PFC-SO: A stirred solution of **PFC-S** (0.54 g, 0.73 mmol) in CHCl₃ (15 mL) was treated with *m*-CPBA (0.63 g, 3.6 mmol) and the reaction mixture was stirred at room temperature for 8 h. Then, the reaction mixture was filtered and washed with CHCl₃. The filtrate was washed with saturated aqueous NaHCO₃ (2 x 25 mL), brine and water respectively. The organic solvent was evaporated and the crude material thus obtained was purified by precipitation in a large excess of cold MeOH from a CHCl₃ solution, to afford the desired polymer as a dark-green solid (0.43 g, 76%).

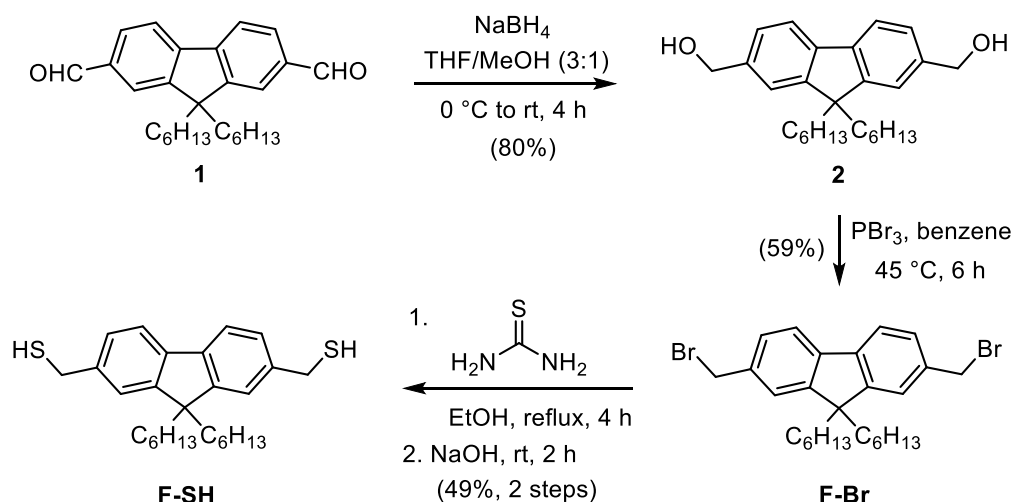
IR (ATR) ν_{\max} (cm⁻¹): 2930, 2823, 1480, 1308, 1110; ¹H NMR (400 MHz, CDCl₃): δ 0.58-0.83 (m, 16H), 0.92-1.29 (m, 28H), 1.88-2.14 (m, 6H), 2.22-2.43 (m, 2H), 4.21 (s, 4H), 4.33 (s, 4H), 4.51-4.71 (m, 1H), 7.15 (d, 2H, $J = 8.2$ Hz), 7.30-7.48 (m, 4H), 7.61 (s, 1H), 7.75 (d, 2H, $J = 7.6$ Hz), 7.80 (s, 1H), 8.05-8.21 (m, 2H); ¹³C NMR (100 MHz, CDCl₃): δ 13.91, 13.94, 22.44, 22.47, 23.91, 26.80, 29.01, 29.63, 31.50, 31.55, 33.74, 40.23, 111.45, 114.03, 120.38, 120.63, 120.84, 121.60, 122.47, 123.83, 124.91, 125.50, 126.73, 129.89, 139.29, 141.14, 142.69, 151.65; λ_{\max} : 249, 259, 275, 287, 317 nm.

Synthesis of PFVCV. In a sealed round bottom flask, a stirred solution of **PFC-SO** (0.2 g, 0.26 mmol) in a 2:1 THF/*t*-BuOH mixture (12 mL) was treated with freshly prepared Al₂O₃-KOH (0.3 g) at 0 °C, then CF₂Br₂ (1.5 mL) was added at the same temperature. The reaction mixture was stirred at room temperature for 24 h, then filtered through celite and washed with CH₂Cl₂. The solvent was evaporated and the crude material purified by precipitation in a large excess of cold MeOH from a CHCl₃ solution, to afford the desired polymer as a yellow solid (32 mg, 43%).

IR (ATR) ν_{\max} (cm⁻¹): 2924, 2853, 1466, 1048, 790; ¹H NMR (400 MHz, CDCl₃): δ 0.64-0.78 (m, 16H), 0.93-1.16 (m, 28H), 1.86-2.06 (m, 6H), 2.23-2.39 (m, 2H), 4.52-4.62 (m, 1H), 7.22-7.32 (m, 3H), 7.40-7.54 (m, 6H), 7.57-7.67 (m, 3H), 7.94-8.06 (m, 2H); λ_{\max} : 265, 427, 452 nm.

RESULTS AND DISCUSSION

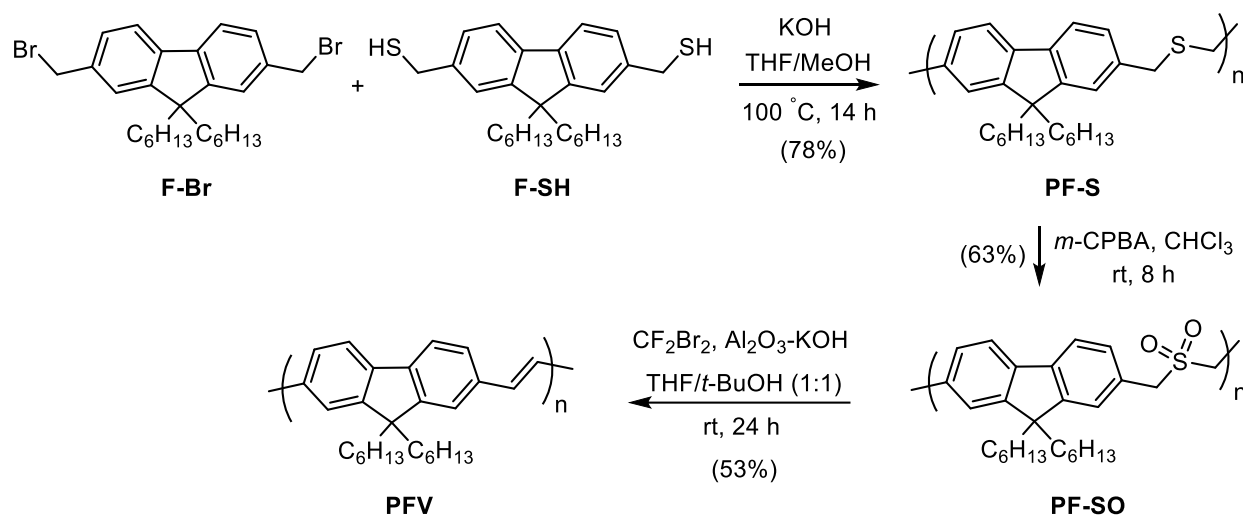
Synthesis and characterization of symmetrical poly(arylene vinylene)s. For our initial studies, we have selected specific monomers, namely, 2,7-bis(bromomethyl)-9,9'-dihexyl-9H-fluorene (**F-Br**) and 2,7-bis(mercaptomethyl)-9,9'-dihexyl-9H-fluorene (**F-SH**) (Scheme 1). The general synthetic strategy to symmetrical PPV's following **Route A** is outlined in Figure 1. 9,9-Dihexylfluorene has been widely employed as a building block for the synthesis of electroluminescent polymers.³⁸⁻⁴⁰ Moreover, fluorene-based polymers exhibit excellent solubility, good charge carrier mobility, and high solid state photoluminescence (PL) quantum yield.⁴¹ Reduction of fluorene-dicarbaldehyde³⁴ (**1**) with NaBH₄ in THF/MeOH⁴² afforded the 2,7-bis(hydroxymethyl)-9,9'-dihexyl-9H-fluorene (**2**) in 80% yield. Treatment of **2** with PBr₃ in benzene³⁵ at 45 °C gave the desired 2,7-bis(bromomethyl)-9,9'-dihexyl-9H-fluorene monomer (**F-Br**) in 59% yield. Subsequent treatment of monomer **F-Br** with thiourea in refluxing EtOH for 4h followed by basic hydrolysis provided the desired monomer, **F-SH** (Scheme 1).³⁶



Scheme 1. Synthesis of monomers 2,7-Bis(bromomethyl)-9,9'-dihexyl-9H-fluorene (**F-Br**) and 2,7-Bis(mercaptomethyl)-9,9'-dihexyl-9H-fluorene (**F-SH**).

The general protocol for the preparation of poly(fluorene vinylene) (**PFV**) is illustrated in Scheme 2. After screening various conditions for the step-growth polymerization of stoichiometric amounts of **F-Br** and **F-SH** (see ESI, Tables S1-4), soluble polymers of rather high apparent molecular weight were obtained in presence of 3 eq. of powdered KOH in THF/MeOH (1:1) at 100 °C for 14 h. These conditions led to poly(fluorene-sulfide)s (**PF-S**) in 78% final yield. Strong, non-nucleophilic 1,1,3,3-tetramethylguanidine (TMG) afforded higher molecular weights and narrower dispersities (see ESI). Due to their lower molecular weight, however, polymers obtained from KOH also proved more soluble. Initial studies on the oxidation of **PF-S** using oxone[®] as the oxidizing agent in MeOH/H₂O were unsuccessful, resulting in a mixture of sulfoxide and sulfone products. In contrast, treatment of 1 eq. of **PF-S** with 5 eq. of *m*-CPBA in CHCl₃ at room temperature for 8 h afforded the polyfluorene-sulfone (**PF-SO**) in 63 % yield. The latter polymer was finally subjected to the Ramberg-Bäcklund reaction using Chan's modified procedure (CF₂Br₂, Al₂O₃-KOH, *t*-BuOH).⁴³ The reaction was however sluggish under these conditions, very likely because of the low solubility of **PF-SO** in *t*-BuOH. We noted that a mixture of

THF and *t*-BuOH (1:1) was more suitable for this reaction. Treatment of **PF-SO** with an excess of CF_2Br_2 and freshly prepared $\text{Al}_2\text{O}_3\text{-KOH}$ in THF/*t*-BuOH (1:1), at room temperature for 24 h, thus gave polymer **PFV** in 53% yield. The three polymers, **PF-S**, **PF-SO** and **PFV** were purified by precipitation using CHCl_3 and MeOH at room temperature.



Scheme 2. Synthesis of poly(fluorene vinylene) (**PFV**) via a three-step procedure involving step-growth polymerization, oxidation and Ramberg-Bäcklund reaction.

Table 1. Size exclusion Chromatography (SEC) analysis of polymers in THF at 25 °C using PS standards for calibration

entry	polymer	$\bar{M}_n^{(a)}$ (g/mol)	$\bar{M}_w^{(a)}$ (g/mol)	$\mathcal{D}^{(a)}$
1	PF-S	7,500	14,300	1.90
2	PF-SO	15,000	32,000	2.10
3	PFV	7,600	13,200	1.70
4	PFC-S	40,700	82,300	2.02
5	PFC-SO	30,400	61,200	2.01
6	PFVCV	5,500	11,400	2.05

(a) Number- and weight-average molar mass (in $\text{g}\cdot\text{mol}^{-1}$) and dispersity determined by size exclusion chromatography in THF (PS calibration).

Characterization of the monomers and related polymers (**PF-S**, **PF-SO**, **PFV**) through IR and ^1H NMR spectroscopies, revealed the expected structures with high purity (Figure 2). The overlay of IR spectra of the different polymers is shown in Figure S1 (ESI). Comparison between IR spectra of **PF-S** and **PF-SO** showed additional absorption bands at 1319, 1100 cm^{-1} , corresponding to the S=O group. During post-functionalization of **PF-SO** into **PFV**, disappearance of the band at 1319 cm^{-1} and a new absorption band at 860 cm^{-1} due to the olefinic moiety was observed, confirming the complete

transformation of the sulfone group. ^1H NMR spectra revealed the presence of methylene protons for monomers **F-Br** and **F-SH** appearing at δ 4.59 (s) and 3.82 (d) ppm, respectively. These signals vanished in the spectrum of **PF-S**, where a single peak at δ 3.68 ppm (Figure 2) was noted. Upon oxidation, the methylene protons of **PF-SO** were shifted downfield to δ 4.20 ppm. Importantly, no signal around δ 3.90 ppm, resulting from a partial oxidation of the sulfide into the sulfoxide was detected.⁴⁴ After treating the **PF-SO** under modified Ramberg-Bäcklund reaction conditions, ^1H NMR of **PFV** revealed a (*E*)-stereoselectivity for the double bonds, a result consistent with observations made for model dibenzylic sulfones reported earlier,^{43,45} and that is in good agreement with spectroscopic data reported by Nomura *et al.* concerning PFV synthesis by ADMET.^{32,33} It is also worth mentioning that we did not observe any residual benzylic protons at δ 4.20 ppm, attesting to the complete conversion of dibenzylic sulfones into olefinic moieties, and to the formation of fully π -conjugated polymers. Average molecular weights were evaluated by size exclusion chromatography (SEC) in THF using polystyrene standards. Results are summarized in Table 1 and SEC traces of **PFV**, **PF-S** and **PF-SO** are shown in Figure 3. The fluorene-based copolymer, **PF-S**, is characterized by a moderate molecular weight for the parent compounds (Table 1, entry 1), increasing after sulfonation (Table 1, entry 2). The final polymer, **PFV**, has a similar molecular weight than its precursor **PF-S** (Table 1, entry 3). After post-chemical modification forming the sulfone and the π -conjugated polymers, M_n and M_w values changed significantly, most likely owing to the variation of solubility of the different polymers. Finally, the high thermal stability of the different polymers (**PF-S**, **PF-SO**, **PFV**) was established by TGA with a loss less than 10% upon heating up to 400 °C (see Figure S6, ESI).

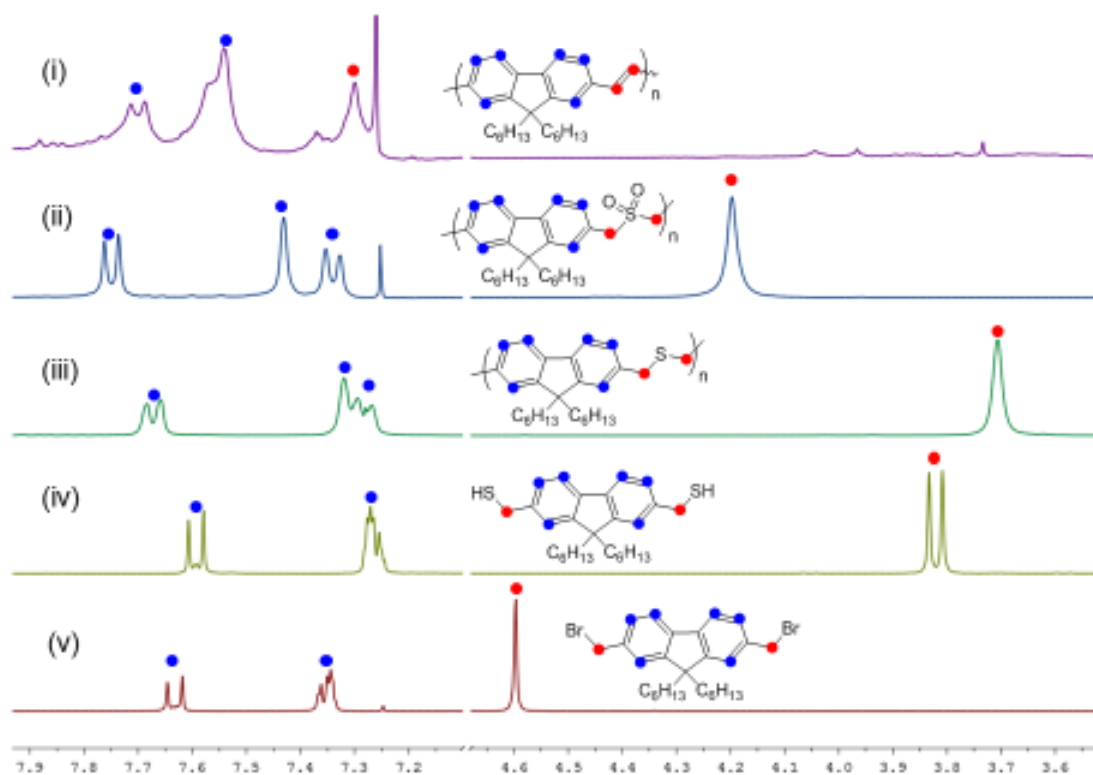


Figure 2. ^1H NMR spectra of (i) **PFV**; (ii) **PF-SO₂**; (iii) **PF-S**; (iv) **F-SH**; (v) **F-Br** in CDCl_3 (400 MHz); *n*-hexyl peaks are omitted for clarity.

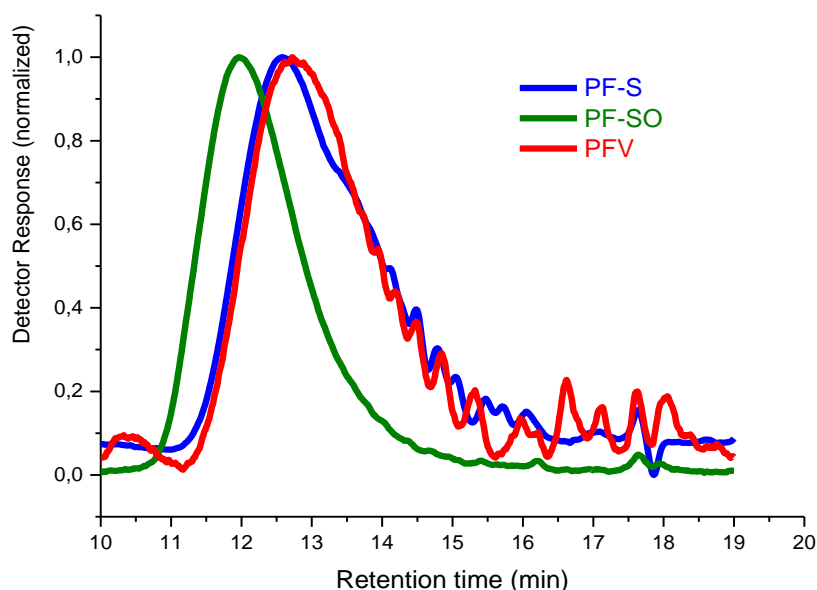
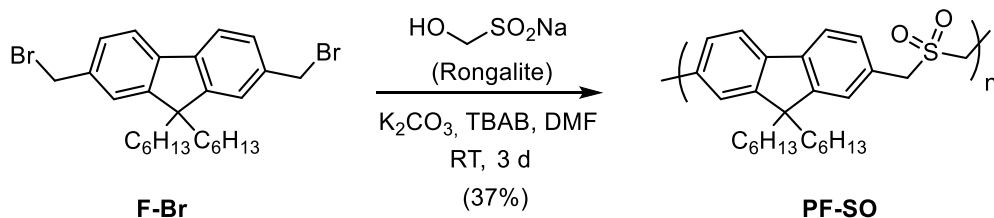


Figure 3. SEC traces in THF (PS standards; RI Detector) of **PFV**, **PF-SO** and **PF-S**.

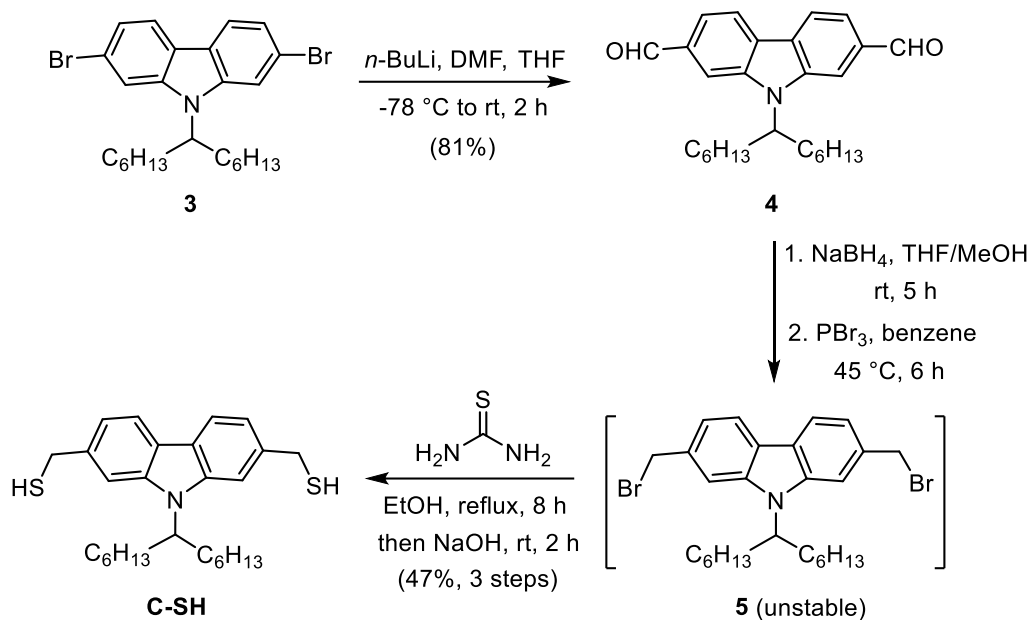
Synthesis of poly(flourene-sulfone)s (**PF-SO**) via the Rongalite[®] route (see Scheme 3).

With a view at developing a simpler and inexpensive protocol for the synthesis of polysulfone-type precursors of the Ramberg-Bäcklund reaction, we envisioned that commercially available rongalite[®],⁴⁶ *i.e.* sodium hydroxymethanesulfinate, could serve as a source of sulfoxylate dianion (SO_2^{2-}). Rongalite[®] is inexpensive and is used as a less oxygen-sensitive bleaching agent than sodium dithionite ($\text{Na}_2\text{S}_2\text{O}_4$), for the synthesis of symmetrical sulfones. Best results were obtained when treated 1 eq. of fluorene-Br (**F-Br**) with rongalite[®] (5 eq.) in the presence of K_2CO_3 (5 eq.) and tetra-*n*-butylammonium bromide (TBAB) (0.5 eq.) as a phase-transfer catalyst in DMF at room temperature for 3 days (Scheme 3). This gave the desired polyfluorene-sulfone (**PF-SO**) with $\bar{M}_n = 2700$ g/mol and $D = 1.7$. Despite a modest isolated yield of 37%, and low molecular weight, this method opens up an easy entry to **PF-SO**, and its application affords an access to symmetrical PPV-like materials in only two-step from readily available benzylic bromides.



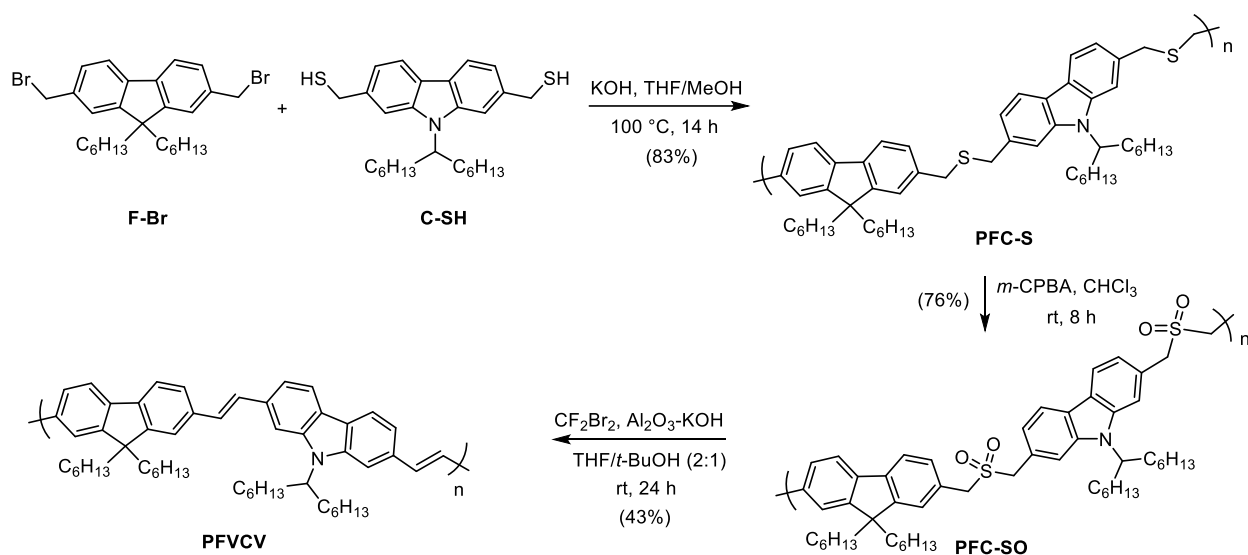
Scheme 3. An access to **PF-SO** using the rongalite[®] route.

Synthesis of unsymmetrical poly(arylene vinylene)s. Based on the above findings, we extended our strategy to the synthesis of unsymmetrical poly(arylene vinylene)s (PAr^{1,2}V's; **route B**, Figure 1). A dithiol-functionalized carbazole derivative (**C-SH**) was thus selected as a co-monomer, the latter being synthesized as shown in Scheme 4.³⁷ Compound **5** being not stable at room temperature, the crude compound was used in the next step without further purification, leading to the desired **C-SH** in 55% yield, after treatment with thiourea and hydrolysis under basic conditions.



Scheme 4. Synthesis of carbazole monomer **C-SH**.

To validate our strategy for the synthesis of alternated poly(arylene vinylene)s (**Route B**, Figure 1), 1 eq. of **F-Br** was treated with 1 eq. of **C-SH** in the presence of 3 eq. of powdered KOH in THF/MeOH at 100 °C for 14 h (Scheme 5). This gave a polysulfide, **PFC-S**, in 83% yield after purification. Oxidation of **PFC-S** with 5 eq. of *m*-CPBA in CHCl₃ at room temperature for 8 h provided the corresponding polysulfone (**PFC-SO**) in 76% yield. Finally, treatment of **PFC-SO** under Ramberg-Bäcklund conditions produced the desired poly(flourene vinylene-*co*-carbazole vinylene) (**PFVCV**) in 43% yield.



Scheme 5. Synthesis of poly(flourene vinylene-*co*-carbazole vinylene) **PFVCV**.

Monomers and polymers (**PFC-S**, **PFC-SO** and **PFVCV**) were characterized by SEC, IR and ^1H NMR spectroscopy. Similar patterns were observed by ^1H NMR, as illustrated in Figure 4. Polysulfides **PFC-S** exhibited high apparent molecular weights (Table 1, entries 4-6). Again, this could be due to an increase of the hydrodynamic volume in THF after sulfonation. Higher molecular weights were achieved for the parent **PVCS** (Table 1, entry 4), but lower values were noted after the two modification steps forming **PFC-SO** and **PFVCV** (Table 1, entries 5-6), respectively (see SEC traces in Figure 5). This could not only be explained by a different solution behavior, but also by possible fractionation during purification by filtration, in agreement with the decrease in dispersity. As above for **PFV**, high thermal stability of the polymers (**PFC-S**, **PFC-SO** and **PFVCV**) was shown by TGA (see Figure S6, ESI).

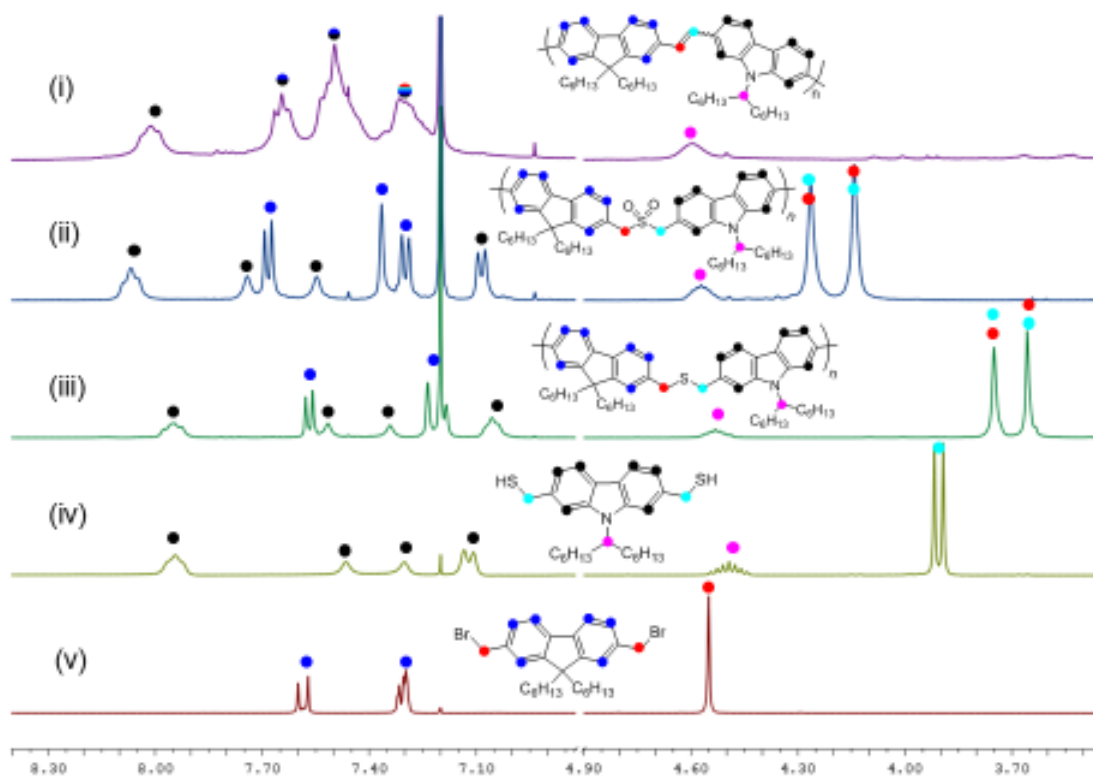


Figure 4. ^1H NMR spectra of (i) PFCV; (ii) PFC-SO; (iii) PFC-S; (iv) C-SH; (v) F-Br in CDCl_3 (400 MHz); The n -hexyl peaks are omitted for clarity.

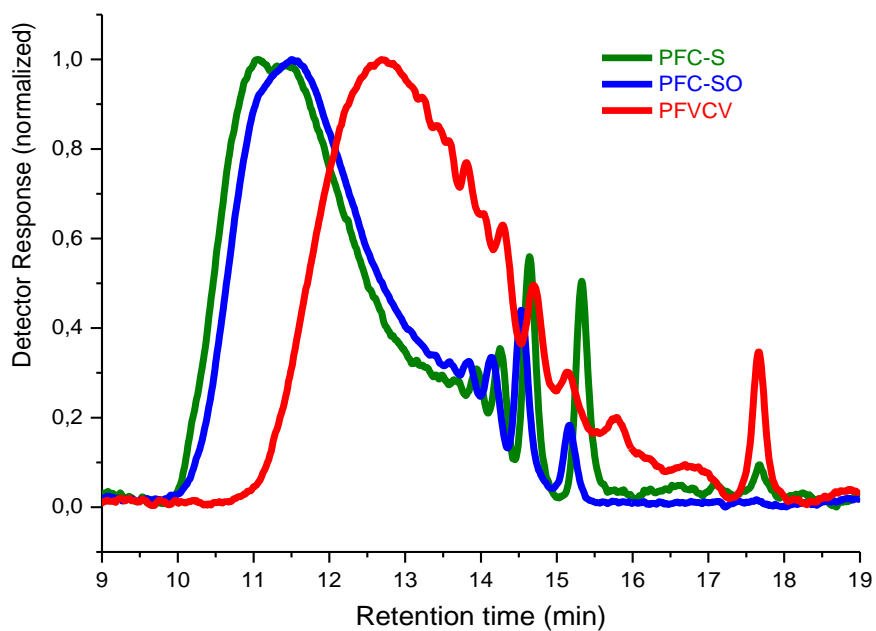
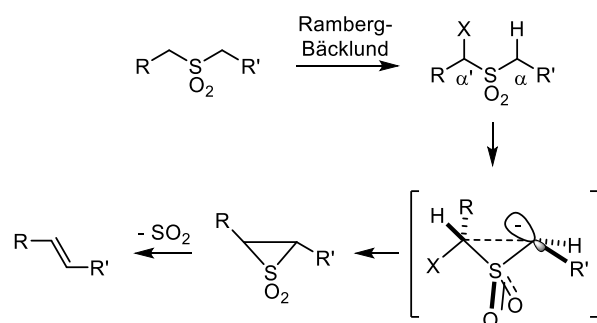


Figure 5. SEC traces in THF of PFCV, PFC-SO and PFC-S.

Overall, this three-step reaction sequence to poly(arylene vinylene)s is efficient and stereoselective, although the Ramberg-Bäcklund reaction step gives moderate yields, particularly when steric hindrance around the olefinic moiety is increasing. This limitation is likely inherent to the Ramberg-Bäcklund reaction, which proceeds through an episulfone intermediate resulting from the displacement of the halogen α' to the sulfonyl group by an α -carbanion (Scheme 6). This process is believed to occur through a semi-W-conformation, the elimination step being rate-limiting.⁴⁷⁻⁴⁸ While this conformation is easily attained in small acyclic systems, this might not be the case with polymeric chains, in which strain and folding might retard the elimination and the subsequent SO_2 extrusion. This might also explain the long reaction time needed in our polymerization experiments, compared to those noted with molecular compounds, and the low conversion with substrates having substituents on the arenes *ortho* to the sulfonyl chain (not described here).



Scheme 6. Conformational requirements in the Ramberg-Bäcklund reaction.

Optical properties. The optical properties of the final (co)polymers were analyzed by UV-Vis absorption and fluorescence spectrophotometry (**PFV**, **PFVCV**) both in solution in chloroform and in bulk on solid thin films. UV-Vis in chloroform are shown for **PFV** (and its precursors **PF-S** and **PF-SO**) on Figure 6, and for **PFVCV** (and its precursors **PFC-S** and **PFC-SO**) on Figure 7. In both cases, a strong red-shift for the two final (co)polymers can be observed. It can be attributed to the extension of the conjugation for **PFV** and **PFVCV**, while their precursors are not π -conjugated. Surprisingly, the two (co)polymers, **PFV** and **PFVCV** showed almost the same UV-Vis pattern in chloroform solution (Figures 6 and 7), exhibiting in both cases two absorption maxima around 425 and 455 nm in solution. These UV data are very similar to those of **PFV** synthesized by the ADMET method, as reported by Namura et al.³³ In other words, alternation with carbazole subunits did not affect optical properties of the material. No significant change was eventually noted in the UV-Vis absorption from thin-films of (co)polymers **PFV** & **PFVCV** (See ESI, Figure S5). The absorption bands were slightly red-shifted relative to that of **PFV** derivatives.⁴⁹ Such small differences can be assigned to the effect of alkyl chains from fluorene repeating units that are shorter in our case, thus favoring π - π stacking and extension of conjugation length. The optical band gaps (E_g) for both polymers, calculated from the onset of the absorption, were approximately 2.6 eV.

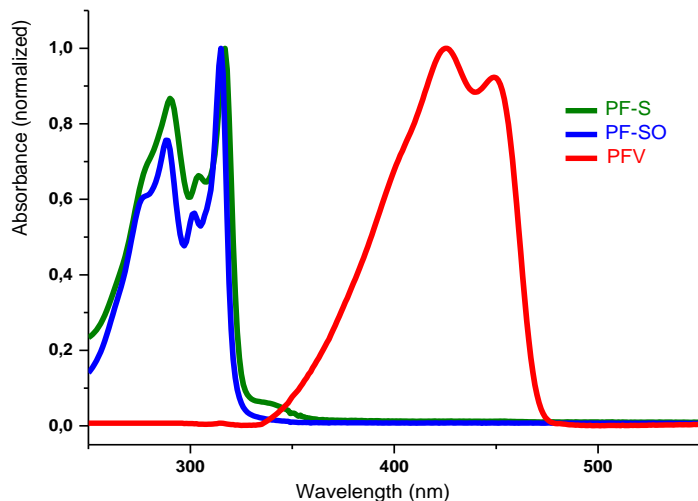


Figure 6. UV-vis absorption of **PF-S**, **PF-SO** and **PFV**

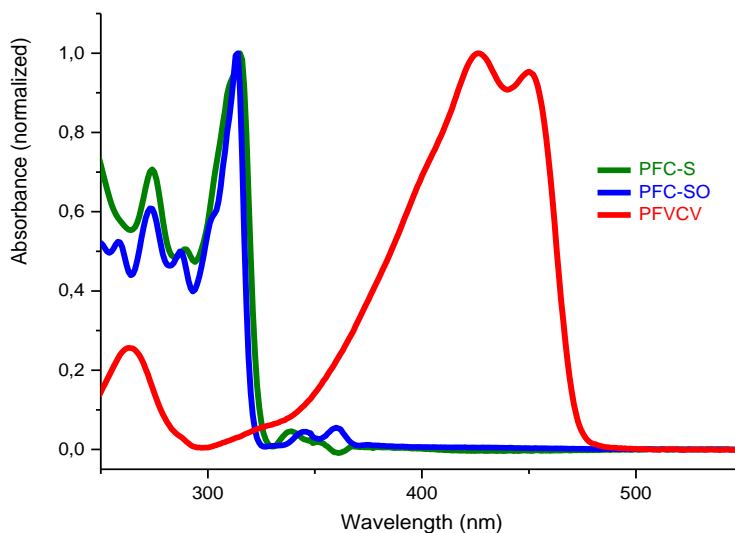


Figure 7. UV-vis absorption of **PFC-S**, **PFC-SO** and **PFVCV**.

Figures 8 and 9 shows the fluorescence spectra recorded with the excitation wavelength corresponding to the two maxima of absorption of the polymers at 425 and 450 nm. In solution, two maxima are observed for both polymers (as well as a slight shoulder) and the corresponding wavelengths are slightly dependent on the wavelength of excitation. For instance, a PFV excitation at 425 nm (Figure 8(a)) led to a strong emission band at 463 nm, then a shoulder at 494 nm and a slight shoulder at 534 nm in excellent agreement with Nomura's emission spectrum recorded at 426 nm (465, 496 and 530 nm respectively).³³ However, in solid state, broad emission peaks can be observed for both, in almost all the visible region and whatever the wavelength of excitation. In solution, both polymer exhibit two maxima of emission at 475 nm and 500 nm. When excited at 450 nm (Figures 8(b) and 9(b)), the second emission

peak was more prominent than when excitation was performed at 425 nm (Figures 8(a) and 9(a)). In solid thin films, both polymers (**PFV** and **PFVCV**) exhibited a broad emission band, even when they were excited at 425 nm (Figures 8(c) and 9(c)) or at 450 nm (Figures 8(b) and 9(b)). However, two main differences can be highlighted between **PFV** and **PFVCV** emission spectra in thin film. First, a more prominent emission peak was noted around 512 nm for **PFVCV** (Figure 9 (c) and 9 (d)), in agreement with reported data on poly(carbazolyl-2,7-vinylene), which is characteristic of a more blueish emitted light as compared to greenish-blue emitted light from **PFV**.⁵⁰ Secondly, the emission band was extended up to 700 nm in the case of **PFV**, compared to 650 nm for **PFVCV**, emphasizing the impact of the carbazolyl vinylene group insertion. This strongest red-shift in solid state for **PFV** could also be explained by a better organization (e.g. π - π stacking) comparing to **PFVCV**. Finally, the quantum yield of the purified **PFV** material, measured upon excitation at 400 nm in THF, reached 40.3% (ESI). Although lower than those found by Nomura et al.,³³ our values are very satisfactory, indicating that the **PFV** prepared through our method is also free of defects, as further supported by the similar absorption and emission maxima (vide supra).

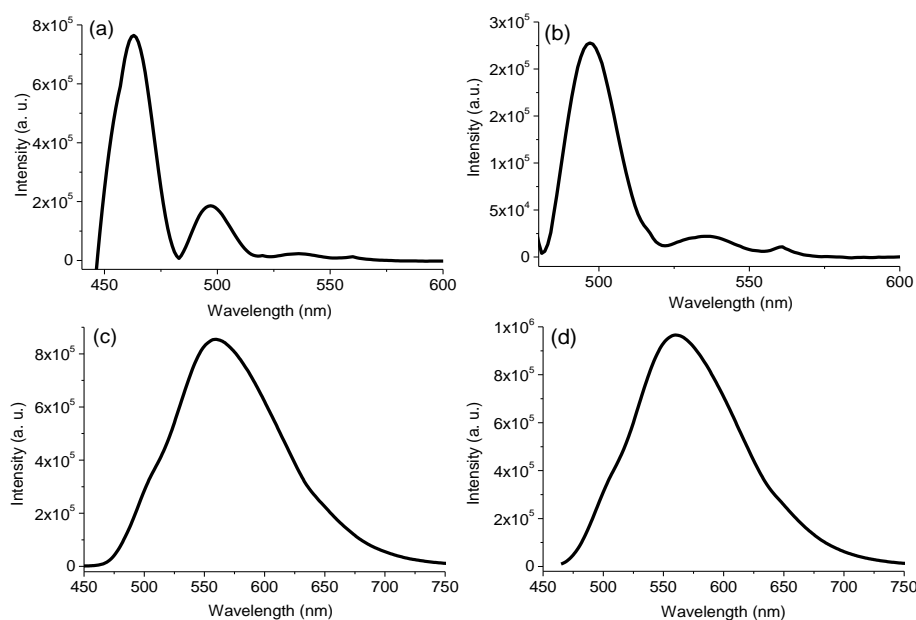


Figure 8. Emission spectra of **PFV**: (a) excited at 425 nm in CHCl_3 ; (b) excited at 450 nm in CHCl_3 ; (c) excited at 420 nm on thin film; (d) excited at 450 nm on thin-film.

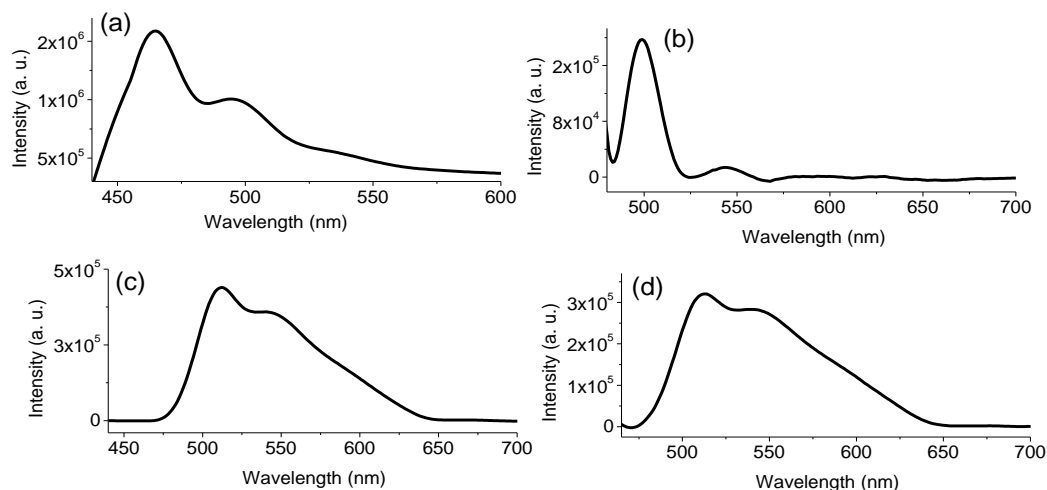


Figure 9. Emission spectra of **PFVCV**: (a) excited at 425 nm in CHCl_3 ; (b) excited at 450 nm in CHCl_3 ; (c) excited at 425 nm on thin film; (d) excited at 450 nm on thin-film.

For quenched poly(fluorene vinylene), **PFVQ**, despite a slight variation of molar masses, there is no significant change in the absorption and emission spectral properties (Figures S3-4, ESI).

Thermal stability. The thermal stability of **PFV** and its precursors (**PF-S**, **PF-SO**) as well as the stability of **PFVCV** were finally analyzed by TGA (See ESI, Figure S6). The two conjugated polymers **PFV** and **PFVCV** are stable until 450 °C. Their precursors (of sulfide- and sulfone-type) are reacting at lower temperatures (between 300 °C and 350 °C) and finally start to decompose at 450 °C.

CONCLUSION

A novel synthetic strategy involving a sulfone-based precursor step-growth polymerization route followed by post-chemical modification *via* the Ramberg-Bäcklund reaction provides an easy access to poly(arylene vinylene)-like semiconductors. The sulfone precursors are easily obtained allowing the connection between electronically differentiated arenes. Symmetrical polysulfones may also be elaborated starting from benzylic bromides precursors and rongalite[®] as a source of sulfoxylate dianion (SO_2^{2-}). Polysulfones and their polysulfide precursors can be equipped with apolar alkyl chains, thus securing their solubility in organic solvents during polymer elaboration, allowing the final purification of the material through precipitation. Further optimization may be needed, in particular to reduce the environmental impact of the reaction sequence. However, such a methodology used to synthesize copolymers composed of carbazolyl and fluorenyl subunits paves the way for the preparation of a plethora of copolymer structures and/or various architectures. We are for instance currently investigating alternation of electron-rich and electron-poor subunits, along with the integration of such materials free of transition metal sources in optoelectronic devices.

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