Polyacetylenes Bearing Chiral-Substituted Fluorene and Terfluorene Pendant Groups: Synthesis and Properties

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ABSTRACT: The synthesis of the first polyacetylenes bearing chiral fluorene-based pendant groups is described. Poly{9,9-bis[(*S*)-3,7-dimethyloctyl]fluoren-2-ylacetylene} (**PFA1**), poly{9,9-bis[(*S*)-2-methylbutyl]-fluoren-2-ylacetylene} (**PFA2**), and poly{9,9,9′,9′,9″,9″-hexakis[(*S*)-2-methylbutyl]-7,2′;7′,2″-terfluoren-2-ylacetylene} (**PFA3**) have been obtained by Rh(I)-catalyzed polymerization of the corresponding terminal acetylene monomers 2-ethynyl-9,9-bis[(*S*)-3,7-dimethyloctyl]fluorene (**2a**), 2-ethynyl-9,9-bis[(*S*)-2-methylbutyl]fluorene **(2b)**, and 2-ethynyl-9,9,9′,9′,9″,9″-hexakis[(*S*)-2-methylbutyl]-7,2′;7′,2″-terfluorene (**10**). The effect of the alkyl chain length at the C-9 position of fluorene on the structural and conformational aspects of the polymers **PFA1** and **PFA2** as well as on their chiroptical properties was studied by XRD, DSC, TGA, GPC, UV−vis, and CD. A more planar conformation of the polyenic backbone of **PFA1** with respect to **PFA2** can be inferred by a red shift of the $\pi-\pi^*$ transition in the UV−vis spectra. Their photoluminescence properties are those typical of fluorene systems. CD measurements evidenced Cotton effects of opposite signs in correspondence of the backbone absorption region, ascribable to an excess of a screw sense of the helical conformations assumed by the two polymers. **PFA3** revealed an amorphous structure and exhibited peculiar thermal stability features (as indicated by TGA and DSC). Its emission spectra interest the violet-blue region and do not show any substantial red shift passing from solution to solid state, thus pointing out an aggregation prevention of terfluorene groups by means of the polyacetylene backbone.

Introduction

Organic π-conjugated systems have been used as active layers in light-emitting diodes (OLED)[1] and show particular features that make them promising candidates for applications in field effect transistors (FET),[2] lasers,[3] and photovoltaic cells.[4] Apart from their primary chemical structure, their optical and electrical properties also depend on their molecular conformation and supramolecular organization in the solid state, parameters which have not yet been completely explored.[5] Depending upon the final application of the material, efforts are being devoted to devising molecular structures either favoring an ordered packing of the π-conjugated molecules or preventing interaction between the systems, if luminescence properties have to be optimized.[6]

Polyfluorenes are among the most promising materials for the construction of full color flat panel displays,[7] owing to their strong electroluminescence (EL) in the blue region. The interest toward these molecules lies in the facile functionalization at the C-9 position which has an influence on solubility as well as on the control of interchain interactions, leaving the effective conjugation length of the emitters unaltered. A major problem in obtaining pure blue EL from substituted oligo- and polyfluorenes is the appearance of a long-wavelength tail in the emission spectra in solid state. This drawback could be the result of aggregate and/or excimer formation as well as of the presence of keto defects[8] under operating conditions and leads to off-white or blue-greenish emission from LEDs fabricated with fluorene derivatives.[9] Research efforts are aiming at minimizing the self-quenching processes of excitons, for example by the introduction of sterically hindered groups,[10] and at increasing the stability in the solid state by raising the glass transition temperature.[11] An alternative approach which has recently been followed is the incorporation of well-defined oligofluorene structures within a saturated polymer chain[12] which makes highly improbable the stacking of conjugated moieties. Indeed, oligofluorenes are obtainable in high purity and show interesting and well-defined optical properties.[13] Unfortunately, oligomers tend to form films of low quality and sometimes need to be deposited onto thin film devices by expensive methods, such as vacuum sublimation. The incorporation of π-conjugated moieties (e.g., oligofluorenes) as pendant moieties of a suitable rigid polymeric backbone (such as a polyacetylene substituted with very bulky pendant groups) may in principle combine the need for a high molecular weight material (necessary for solution processability) with avoiding aggregate formation. The only examples in this respect count oligo(phenylenevinylene)s[14] and substituted siloles[15] as pendant groups of polyacetylenes.

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Polyacetylenes are considered the prototypes of the π-conjugated organic materials,[16] and to date, several properties of these macromolecules have been investigated.[17−19] While the applications of polyacetylenes have been very limited, the discovery of efficient and stereospecific rhodium(I) catalysts for arylacetylene polymerization[20] led to the blooming of studies aimed at elucidating the relation between properties of poly(arylacetylene)s and their backbone arrangement.[21] It has been reported that suitable choice of Rh(I) catalyst produces highly stereoregular cis-transoidal backbone configurations, to which are associated not only the important secondary helical structure but also a quaternary columnar aggregation.[22] Moreover, it is known that polyacetylenes obtained by Rh(I) polymerization of chiral functionalized acetylenes may assume a helical conformation with one predominant helix sense.[23] Although the cis-transoidal polyenic backbone is not an efficient emitter, these macromolecules may have potential chiral recognition properties.[24]

Our research aims at synthesizing oligofluorene-functionalized polyacetylenes to study how the secondary structure of the backbone influences the spatial disposition of the fluorene luminophores. Therefore, we have synthesized and polymerized two monofluorenylacetylene monomers substituted with the chiral [(*S*)-2-methylbutyl] and [(*S*)-3,7-dimethyloctyl] chains in the C-9 position. The obtained polymers were investigated by XRD, TGA, DSC, GPC, IR, UV−vis, and PL. The presence of the chiral moieties allowed the investigation of the secondary helical arrangement of the polyenic backbone by circular dichroism measurements. As an extension of the model systems toward materials potentially applicable to thin film devices, a comparative study was performed on the polymer obtained by Rh(I) polymerization of a terfluorenylacetylene monomer functionalized with the C_5 chiral alkyl chains.

Experimental Section

All manipulations have been carried out under an inert nitrogen atmosphere using common Schlenk techniques and freshly distilled solvents. ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-500. UV−vis spectra were recorded on a Kontron Uvikon 942, and fluorescence spectra were obtained on a Varian Cary Eclipse spectrofluorimeter. FT-IR spectra were recorded on a Bruker Vector 22 spectrometer. CD spectra were recorded with a Jasco J-810 spectropolarimeter. Mass spectra were obtained on a HP 5973 instrument. GPC analyses were carried out on a HP 1050 instrument equipped with a Pl-gel 5 mm mixed-D 300 mm × 7.5 mm column. THF solutions for GPC analysis were eluted at 25 °C at a flow rate of 1 mL/min and analyzed using a multiple wave detector [λ = 320 and 350 nm]. Molecular weights and molecular weight distributions are reported relative to polystyrene standards. Thermogravimetric analyses (TGA) were carried out with a thermobalance TA Instruments 2590; differential scanning calorimetry (DSC) was measured on a TA Instruments 2920 calorimeter. Both thermal analyses were carried out under a nitrogen flow and with a heating scan of 10 °C/min. X-ray diffraction (XRD) measurements were carried out with an imaging plate (at the distance of 10 cm from the substances) with a 20 mA current and a 40 kV voltage, using Ni-filtered Cu Kα radiation. Specific rotations ($[\alpha]_D$) were measured on a Perkin-Elmer 343 polarimeter with a sodium lamp as light source. 2-Bromo-9,9-bis[(*S*)-3,7-dimethyloctyl]fluorene, 2-bromo-9,9-bis[(*S*)-2-methylbutyl]fluorene, and 2,7-dibromo-9,9-bis[(*S*)-2-methylbutyl]fluorene have been synthesized according to literature procedures.[25]

9,9-Bis[(*S*)-3,7-dimethyloctyl]fluoren-2-ylethynyltrimethylsilane (1a). 2-Bromo-9,9-bis[(*S*)-3,7-dimethyloctyl]fluorene (1.950 g, 3.70 mmol), $PdCl_2(PPh_3)_2$ (52.0 mg, 0.074 mmol), CuI (7.0 mg, 3.7×10^{-2} mmol), and PPh_3 (38.5 mg, 0.15 mmol) were dissolved in diethylamine (20 mL), and then trimethylsilylacetylene (0.436 g, 4.44 mmol) was added to the solution. The reaction mixture was refluxed overnight. After cooling the solution, the solvent was removed under reduced pressure and diethyl ether (100 mL) was added. The solution was filtered, washed with water (3 × 80 mL), and dried over Na_2SO_4. The residue was purified by column chromatography (SiO_2, *n*-hexane) to yield **1a** (1.560 g, 78%) as a colorless oil.

^1H NMR (500 MHz, $CDCl_3$): δ 7.39−7.65 (m, 4H), 7.27−7.33 (m, 3H), 1.97 (m, 4H), 0.31−1.46 (38H, alkyl), 0.26 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.1, 150.8, 142.2, 140.5, 131.3, 127.8, 127.1, 126.6, 123.1, 120.2, 119.7, 110.1, 106.1, 94.7, 55.1, 39.4, 37.7, 36.9, 36.7, 33.1, 30.6, 28.1, 24.8, 22.8, 19.7, 0.1. IR (CsI): υ [cm^{-1}] 3064, 2954, 2868, 2156 (−C≡C−), 1451, 1249, 907, 843, 759, 738. MS (70 eV): [*m*/*z*] 542 (M^+, 55), 401 (4), 261 (18), 245 (11), 73 (37), 57 (33), 43 (100).

9,9-Bis[(*S*)-2-methylbutyl]fluoren-2-ylethynyltrimethylsilane (1b). 2-Bromo-9,9-bis[(*S*)-2-methylbutyl]fluorene (1.350 g, 3.50 mmol), $PdCl_2(PPh_3)_2$ (49.0 mg, 0.07 mmol), CuI (6.7 mg, 3.5×10^{-2} mmol), and PPh_3 (36.7 mg, 0.14 mmol) were dissolved in diethylamine (20 mL), and then trimethylsilylacetylene (0.415 g, 4.20 mmol) was added to the solution. The reaction mixture was refluxed overnight. After cooling the solution, the solvent was removed under reduced pressure and diethyl ether (100 mL) was added. The solution was filtered, washed with water (3 × 80 mL), and dried over Na_2SO_4. The residue was purified by column chromatography (SiO_2, petroleum ether 40−60 °C) to afford **1b** (1.200 g, 85%) as a colorless oil.

^1H NMR (500 MHz, $CDCl_3$): δ 7.25−7.70 (m, 7 H, arom), 1.75−2.10 (m, 4 H), 0.71−0.94 (m, 4H), 0.52−0.60 (m, 8 H), 0.23 (s, 9 H), 0.13−0.23 (m, 6 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.0, 150.6, 141.6, 140.4, 131.1, 127.3, 127.0, 126.8, 123.9, 120.0, 119.4, 110.1, 106.2, 93.5, 54.6, 48.0, 47.8, 31.3, 30.8, 20.9, 20.6, 10.9, 0.1. IR (CsI): υ [cm^{-1}] 3065, 2960, 2874, 2156 (−C≡C−), 1451, 1250, 888, 843, 760, 740. MS (70 eV): [*m*/*z*] 402 (M^+, 88), 331 (94), 275 (99), 261 (99), 73 (100), 43 (31).

2-Ethynyl-9,9-bis[(*S*)-3,7-dimethyloctyl]fluorene (2a). **1a** (1.560 g, 2.88 mmol) was dissolved in CH_2Cl_2 (10 mL), and to the solution, kept under vigorous stirring, were added KF (0.864 g, 14.40 mmol) and methanol (10 mL). The mixture was refluxed for 4 h. After cooling the solution, the solvent was removed under reduced pressure, and diethyl ether (50 mL) was added to the residue. The obtained suspension was filtered, washed with water (3 × 50 mL), and dried over Na_2SO_4. After solvent removal in vacuo, the crude was purified by column chromatography (SiO_2, petroleum ether 40−60 °C) to afford **2a** (1.136 g, 84%) as a colorless oil.

^1H NMR (500 MHz, $CDCl_3$): δ 7.61−7.72 (m, 2H), 7.43−7.50 (m, 2H), 7.29−7.36 (m, 3H), 3.12 (s, 1H, ≡C−H), 1.96 (m, 4H), 0.36−1.48 (38H, alkyl). ^{13}C NMR (125 MHz, $CDCl_3$): δ 151.1, 150.8, 142.2, 140.5, 131.3, 127.8, 127.1, 126.6, 123.1, 120.2, 119.7, 110.0, 87.6, 85.0, 55.1, 39.4, 37.8, 36.7, 36.5, 33.0, 30.4, 28.1, 25.0, 22.6, 19.7. IR (CsI): υ [cm^{-1}] 3313 (≡C−H), 3065, 2954, 2868, 2106 (−C≡C−), 1466, 1366, 831, 738. MS (70 eV): [*m*/*z*] 470 (M^+, 6), 231 (12), 203 (32), 189 (100), 71 (13), 57 (25), 43 (98). Elem Anal. Calcd: C, 89.29%; H, 10.71%. Found: C, 89.70%; H, 10.30%. UV−vis: λ_{max} [nm] 316 (ϵ = 41 830 mol^{-1} L cm^{-1}), 304 (ϵ = 29 020 mol^{-1} L cm^{-1}), 291 (ϵ = 40 250 mol^{-1} L cm^{-1}); $[\alpha]_D$ + 0.08° (*c* = 1.00 g/dL in $CHCl_3$ at room temperature).

2-Ethynyl-9,9-bis[(*S*)-2-methylbutyl]fluorene (2b). **1b** (1.200 g, 2.98 mmol) was dissolved in CH_2Cl_2 (10 mL), and to the solution, kept under vigorous stirring, were added KF (0.866 g, 14.90 mmol) and methanol (10 mL). The mixture was refluxed for 4 h. After cooling the solution, the solvent was removed under reduced pressure and diethyl ether (50 mL) was added to the residue. The obtained suspension was filtered, washed with water (3 × 50 mL), and dried over Na_2SO_4. After solvent removal in vacuo, the crude was purified by column chromatography (SiO_2, petroleum ether 40−60 °C) to afford **2b** (0.880 g, 89%) as a colorless oil.

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.63−7.70 (m, 2H), 7.46−7.50 (m, 2H), 7.27−7.38 (m, 3H), 3.11 (s, 1H, ≡C−H), 2.05−2.12 (m, 2H), 1.81−1.87 (m, 2H), 0.74−0.95 (m, 4H), 0.54−0.61 (m, 8H), 0.18−0.24 (m, 6H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 151.2, 150.9, 142.2, 140.6, 131.3, 127.7, 127.4, 127.1, 124.2, 120.3, 119.8. 110.1, 87.6, 85.0, 54.9, 48.2, 48.0, 31.3, 30.8, 21.2, 21.0, 11.2. IR (CsI): υ [cm^{-1}] 3310 (≡C−H), 3064, 2959, 2872, 2106 (−C≡C−), 1450, 1378, 779, 740. MS (70 eV): [*m/z*] 330 (M$^+$, 98), 259 (97), 203 (99), 189 (100), 71 (8), 57 (20), 43 (26). Elem Anal. Calcd: C, 90.85%; H, 9.15%. Found: C, 90.72%; H, 9.28%. UV−vis: λ_{max} [nm] 317 (ϵ = 31 970 mol^{-1} L cm^{-1}), 304 (ϵ = 22 870 mol^{-1} L cm^{-1}), 291 (ϵ = 32 130 mol^{-1} L cm^{-1}); [α]$_D$ + 0.12° (*c* = 1.00 g/dL in CHCl$_3$ at room temperature).

Poly{9,9-bis[(*S*)-3,7-dimethyloctyl]fluoren-2-ylacetylene} (PFA1). A 50 mL round-bottom flask was charged with [Rh(nbd)Cl]$_2$ (2.44 mg, 0.53 × 10^{-2} mmol) and triethylamine (1.5 mL), and the obtained solution was stirred for 15 min. Subsequently, a solution of **2a** (0.250 g, 0.53 mmol) in THF (2.0 mL) was added. The color of the solution turned instantly from light yellow to dark brown. The reaction mixture was stirred for 24 h. The polymer was isolated by adding the reaction mixture dropwise to a beaker containing 200 mL of methanol kept under stirring and filtering the resulting suspension. The orange solid was washed with ethanol and dried under vacuum (61%). IR (KBr): υ [cm^{-1}] 3056, 2976, 2868, 1458, 1259, 1091, 1018, 798, 740.

Poly{9,9-bis[(*S*)-2-methylbutyl]fluoren-2-ylacetylene} (PFA2). The reaction was carried out under the same conditions reported for **PFA1** {**2b** (0.200 g, 0.61 mmol), [Rh(nbd)-Cl]$_2$ (2.81 mg, 0.61 × 10^{-2} mmol), TEA (1.5 mL), and THF (2.3 mL)} affording a brown solid (50%). IR (KBr): υ [cm^{-1}] 3056, 2962, 2868, 1458, 1369, 1091, 1002, 834, 740.

2-Bromo-9,9-bis[(*S*)-2-methylbutyl]fluoren-7-yltrimethylsilane[26] **(3).** 2,7-Dibromo-9,9-bis[(*S*)-2-methylbutyl]fluorene (4.035 g, 8.70 mmol) was dissolved in dry THF (65 mL), and to the solution, kept under vigorous stirring at about −80 °C, *n*-BuLi (1.6 M in hexane, 5.4 mL, 8.70 mmol) was added dropwise. After 1 h stirring, Me$_3$SiCl (1.3 mL, 1.086 g, 10.00 mmol) was slowly added. The solution was allowed to warm to room temperature and let to react overnight. After removing the solvent in vacuo, petroleum ether (50 mL) was added. The organic layer was washed with water (3 × 50 mL) and dried over Na$_2$SO$_4$. The product was purified by column chromatography (SiO$_2$, petroleum ether 40−60 °C) to afford **3** (3.700 g, 93%) as a colorless oil.

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.54−7.66 (m, 2H), 7.42−7.51 (m, 4H), 2.02−2.16 (m, 2H), 1.73−1.89 (m, 2H), 0.73−0.99 (m, 4H), 0.50−0.63 (m, 8H), 0.19−0.30 (m, 15H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 153.3, 149.4, 140.9, 140.4, 139.3, 132.0, 130.1, 129.1, 127.3, 121.3, 121.3, 119.2, 55.1, 48.0, 47.5, 31.5, 31.2, 30.7, 21.7, 21.1, 11.2, −0.8.

2-Trimethylsilyl-9,9-bis[(*S*)-2-methylbutyl]fluoren-7-ylboronic Acid[26] **(4).** To a solution of **3** (3.300 g, 7.20 mmol) in dry THF (55 mL), kept under vigorous stirring at about −80 °C, *n*-BuLi (1.6 M in hexane, 5.0 mL, 8.00 mmol) was added dropwise. After 1 h stirring, tri(isopropyl)borate (2.5 mL, 2.012 g, 10.70 mmol) was added in one portion. The solution was allowed to warm to room temperature and let to react overnight. After removing the solvent in vacuo, water (50 mL) was added to the crude, and the product was extracted with diethyl ether (3 × 50 mL). The organic layer was washed with brine (150 mL) and dried over Na$_2$SO$_4$. After removing the solvent in vacuo, the residue was purified by column chromatography (SiO$_2$, petroleum ether 40−60 °C/ethyl acetate = 60/40, yielding **4** (2.010 g, 66%) as white solid.

^{1}H NMR (500 MHz, CDCl$_3$): δ 8.24−8.29 (m, 2H), 7.89 (d, *J* = 0.57 Hz, 1H), 7.79 (d, *J* = 7.37 Hz, 1H), 7.59 (s, 1H), 7.53 (d, *J* = 7.37, 1H), 2.20−2.36 (m, 2H), 1.93−2.01 (m, 2H), 0.86−1.06 (m, 4H), 0.54−0.71 (m, 8H), 0.23−0.35 (m, 15H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 150.5, 150.1, 145.6, 141.4, 139.5, 134.3, 132.1, 131.7, 130.9, 129.0, 119.5, 119.3, 54.5, 47.8, 47.5, 31.4, 31.1, 30.6, 21.6, 21.4, 11.0, −1.0.

9,9,9′,9′-Tetrakis[(*S*)-2-methylbutyl]-7,2′-bifluoren-2-yltrimethylsilane (5). A 100 mL three-necked round-bottom flask was charged with **4** (1.140 g, 2.70 mmol), 2-bromo-9,9-bis[(*S*)-2-methylbutyl]fluorene (1.040 g, 2.70 mmol), Pd(PPh$_3$)$_4$ (35.0 mg, 3.0 × 10^{-2} mmol), toluene (6.0 mL), and 3.5 mL of Na$_2$CO$_3$ (2.0 M) solution. The reaction mixture was stirred at 90 °C for 2 days. The solution was cooled to room temperature, and *n*-hexane (20 mL) was added. The organic layers were washed with water (3 × 20 mL) and dried over Na$_2$SO$_4$. After solvent removal in vacuo, the product was purified by column chromatography (SiO$_2$, *n*-hexane/CH$_2$Cl$_2$ = 95/5), yielding **5** (1.630 g, 81%) as a white solid.

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.70−7.80 (m, 4H), 7.59−7.63 (m, 4H), 7.54 (s, 1H), 7.50 (d, *J* = 7.32 Hz, 1H), 7.39 (d, *J* = 7.32 Hz, 1H), 7.35 (d, *J* = 7.32, Hz, 1H), 7.29 (td, *J* = 7.32, 1.22 Hz, 1H), 2.12−2.23 (m, 4H), 1.85−1.95 (m, 4H), 0.78−1.01 (m, 8H), 0.57−0.71 (m, 16H), 0.25−0.33 (m, 21H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 151.6, 151.1, 150.1, 141.2, 140.6, 131.9, 129.1, 127.0, 126.8, 126.1, 124.1, 122.9, 120.0, 119.1, 55.0, 48.2, 47.7, 31.3, 30.7, 21.6, 21.3, 11.2, −0.7; mp 56−58 °C.

2-Iodo-9,9,9′,9′-tetrakis[(*S*)-2-methylbutyl]-7,2′-bifluorene (6). A 50 mL round-bottom flask was charged with **5** (1.470 g, 2.15 mmol) and CH$_2$Cl$_2$ (12 mL). To this solution, kept under stirring at 0 °C, ICl (1.0 M in methylene chloride, 2.5 mL) was added dropwise. The reaction mixture was stirred for 1 h at room temperature. The excess ICl was eliminated by adding dropwise an aqueous solution of Na$_2$S$_2$O$_3$ (5 wt %) until the color of the solution disappeared. The product was extracted with CH$_2$Cl$_2$, and the organic layer was dried over Na$_2$SO$_4$. The residue was purified by column chromatography (SiO$_2$, *n*-hexane/CH$_2$Cl$_2$ = 95/5) to yield **6** (1.550 g, 97%) as a white solid.

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.71−7.79 (m, 4H), 7.67 (dd, *J* = 7.93, 1.22 Hz, 1H), 7.57−7.62 (m, 4H), 7.49 (d, *J* = 7.93 Hz, 1H), 7.39 (d, *J* = 7.32 Hz, 1H), 7.35 (td, *J* = 7.32, 1.22 Hz, 1H) 7.29 (t, *J* = 7.32 Hz, 1H), 2.07−2.23 (m, 4H), 1.80−1.95 (m, 4H), 0.79−1.01 (m, 8H), 0.56−0.72 (m, 16H), 0.24−0.34 (m, 12H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 153.4, 151.2, 150.8, 150.6, 140.9, 140.6, 139.9, 139.2, 135.8, 133.1, 127.1, 126.8, 126.6, 126.1, 125.9, 123.9, 122.5, 121.4, 120.0, 119.8, 54.9, 54.7, 47.9, 47.7, 47.3, 31.1, 30.5, 21.4, 21.0, 11.0; mp 51−53 °C.

9,9,9′,9′,9″,9″-Hexakis[(*S*)-2-methylbutyl]-7,2′;7′,2″-terfluoren-2-yltrimethylsilane (7). The preparation of **7** followed the same procedure reported for **5** starting from **6** and **4** [**6** (1.500 g, 2.00 mmol), **4** (0.842 g, 2.00 mmol), Pd(PPh$_3$)$_4$ (25.0 mg, 2.15 × 10^{-2} mmol), toluene (5.0 mL), Na$_2$CO$_3$ 2.0 M solution (2.5 mL)]. The product was obtained as a white solid in 56% yield.

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.77−7.83 (m, 3H), 7.71−7.76 (m, 2H), 7.61−7.66 (m, 9H), 7.54 (s, 1H), 7.51 (dd, *J* = 7.38, 0.98 Hz, 1H), 7.40 (d, *J* = 7.38 Hz, 1H), 7.36 (td, *J* = 7.38, 0.98 Hz, 1H), 7.29 (td, *J* = 7.38, 1.48 Hz, 1H), 2.14−2.28 (m, 6H), 1.86−1.99 (m, 6H), 0.80−1.05 (m, 12H), 0.58−0.73 (m, 24H), 0.27−0.37 (m, 27H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 151.7, 151.4, 151.0, 150.0, 141.2, 140.6, 140.4, 138.5, 131.9, 129.1, 127.0, 126.7, 126.1, 124.1, 122.8, 120.1, 119.1, 54.9, 48.2, 47.7, 31.4, 30.7, 21.8, 21.3, 11.3, −0.8.

2-Iodo-9,9,9′,9′,9″,9″-hexakis[(*S*)-2-methylbutyl]-7,2′;7′,2″-terfluorene (8). The preparation of **8** followed the same procedure reported for **6** starting from **7** [**7** (1.110 g, 1.12 mmol), ICl (1.0 M in CH$_2$Cl$_2$, 1.5 mL), CH$_2$Cl$_2$ (6 mL)]. The product was obtained as a pale yellow solid in 94% yield.

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.72−7.83 (m, 6H), 7.59−7.70 (m, 9H), 7.49 (d, *J* = 7.88 Hz, 1H), 7.27−7.41 (m, 3H), 2.08−2.28 (m, 6H), 1.81.1.98 (m, 6H), 0.81−1.02 (m, 12H), 0.58−0.73 (m, 24H), 0.26−0.36 (m, 18H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 153.6, 151.7, 150.9, 141.1, 140.9, 140.5, 140.2, 139.4, 136.0, 133.3, 127.4, 127.0, 126.8, 126.3, 124.3, 124.1, 122.8, 121.6, 120.1, 55.2, 54.9, 48.0, 47.9, 31.4, 30.8, 21.7, 21.3, 11.2.

9,9,9′,9′,9″,9″-Hexakis[(*S*)-2-methylbutyl]-7,2′;7′,2″-terfluoren-2-ylethynyltrimethylsilane (9). The synthesis of **9** followed the same procedure reported for **1a** starting from **8** [**8** (1.060 g, 1.02 mmol), PdCl$_2$(PPh$_3$)$_2$ (14.0 mg, 0.02 mmol), CuI (2.0 mg, 0.01 mmol),PPh$_3$ (10.7 mg, 0.04 mmol), NHEt$_2$ (5.5 mL), and trimethylsilylacetylene (0.120 g, 1.22 mmol)]. The product was obtained as a pale yellow solid in 80% yield.

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.72−7.84 (m, 5H), 7.58−7.68 (m, 9H), 7.47−7.50 (m, 2H), 7.27−7.41 (m, 3H), 2.09−2.28 (m, 6H), 1.83−1.98 (m, 6H), 0.81−1.03 (m, 12H), 0.57−0.79 (m, 24H), 0.25−0.37 (m, 27H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 151.8, 151.4, 151.2, 142.2, 141.1, 140.5, 140.1, 139.7, 131.4, 127.8, 127.4, 127.1, 126.8, 126.5, 124.4, 124.0, 122.8, 120.9, 120.5, 120.3, 119.7, 85.0, 55.0, 48.0, 47.8, 31.3, 30.8, 21.8, 21.2, 11.2, 0.1. IR (KBr): υ [cm^{-1}] 3057, 2958, 2836, 2153 (−C≡C−), 1460, 1249, 888, 844, 816, 757.

2-Ethynyl-9,9,9′,9′,9″,9″-hexakis[(*S*)-2-methylbutyl]-7,2′;7′,2″-terfluorene (10). The synthesis of **10** followed the same procedure reported for **2a** starting from **9** [**9** (0.750 g, 0.74 mmol), KF (0.220 g, 3.75 mmol), CH$_2$Cl$_2$ (4 mL), and methanol (4 mL)]. The product was obtained as a white solid in 70% yield.

^{1}H NMR (500 MHz, CDCl$_3$): δ 7.72−7.84 (m, 5H), 7.60−7.71 (m, 9H), 7.50−7.53 (m, 2H), 7.27−7.41 (m, 3H), 3.14 (s, 1H −C≡CH), 2.09−2.28 (m, 6H), 1.83−1.98 (m, 6H), 0.80−1.04 (m, 12H), 0.57−0.78 (m, 24H), 0.26−0.37 (m, 18H). ^{13}C NMR (125 MHz, CDCl$_3$): δ 151.9, 151.4, 151.1, 142.0, 141.1, 140.3, 140.2, 139.7, 131.4, 127.7, 127.4, 127.0, 126.8, 126.3, 124.4, 124.1, 122.8, 120.9, 120.5, 120.2, 119.9, 85.0, 55.0, 48.2, 47.8, 31.4, 30.8, 21.7, 21.2, 11.2. IR (KBr): υ [cm^{-1}] 3310 (≡C−H), 3061, 2957, 2860, 2106 (−C≡C−), 1460, 1376, 816, 741; mp 70−73 °C; Elem Anal. Calcd: C, 90.77%; H, 9.23%. Found: C, 90.51%; H, 9.49%. UV−vis: $\lambda_{\max}$ [nm] 353 (ϵ = 87 190 mol^{-1} L cm^{-1}); [α]$_D$ + 0.16° (c = 1.00 g/dL in CHCl$_3$ at room temperature).

Poly{9,9,9′,9′,9″,9″-hexakis[(*S*)-2-methylbutyl]-7,2′;7′,2″-terfluoren-2-ylacetylene} (PFA3). A 50 mL round-bottom flask was charged with [Rh(nbd)Cl]$_2$ (5.50 mg, 0.012 mmol) and triethylamine (2.0 mL), and the obtained solution was stirred for 15 min. Subsequently, a solution of **10** (0.110 g, 0.12 mmol) in toluene (40 mL) was added. The color of the solution turned from light yellow to dark brown. The reaction mixture was stirred for 24 h. The polymer was precipitated by adding the reaction mixture dropwise to a beaker containing 200 mL of methanol kept under stirring. The suspension was filtered, and the solid was washed with ethanol, affording the product as a brown powder (79%).

IR (KBr): υ [cm^{-1}] 3058, 2957, 2870, 1460, 1376, 1261, 1097, 1020, 814, 740.

Results and Discussion

The monomers used for this study are reported in Scheme 1. **2a** and **2b**, embodying a monofluorene unit, have been prepared to obtain the corresponding polymers as model systems. The different chiral alkyl chains at the C-9 position of the fluorene were chosen in order to investigate the influence of different steric hindrances on the final properties of the macromolecules obtained by Rh(I) polymerization. The presence of a chiral center onto the alkyl chain was devised to investigate the secondary helical arrangement of the functionalized polyenic backbone: the chiral center may in fact induce an excess of one of the screw senses of the helix that can be deduced from the chiroptical properties of the macromolecule.[27] Monomer **10**, embodying a terfluorene moiety, was synthesized in order to move a first step toward the potential extension of the scope of the reaction to more extended fluorene oligomers as emitting materials.

Monomers Synthesis. The synthetic route for monomers **2a** and **2b** is outlined in Scheme 1a. 2-Bromofluorene was first functionalized with the suitable alkyl bromides to obtain the corresponding bis-alkyl derivatives. The syntheses were completed by introduction of the terminal acetylene groups by means of palladium-catalyzed Sonogashira coupling between the relevant fluorenyl bromide and trimethylsilylacetylene, followed by deprotection with potassium fluoride. The presence of the terminal acetylene was confirmed by the IR stretching frequencies at 3313 and 2106 cm^{-1} (**2a**) and 3310 and 2106 cm^{-1} (**2b**) as well as by the ^{1}H NMR resonance at δ 3.12 (**2a**) and δ 3.11 (**2b**).

Table 1. Polymerization of 2a and 2b (Conditions: [Monomer]/[Rh] = 100; *t* = 24 h) and Polymerization of 10 (Conditions: [Monomer]/[Rh] = 10; *t* = 24 h)

monomer	polymer	solvent	yield (%)	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	color
2a	**PFA1**	THF/Et$_3$N	61	70 000	1.9	orange
2b	**PFA2**	THF/Et$_3$N	56	100 000	1.9	brown
10	**PFA3**	toluene/Et$_3$N	79	6 000	4.0	brown

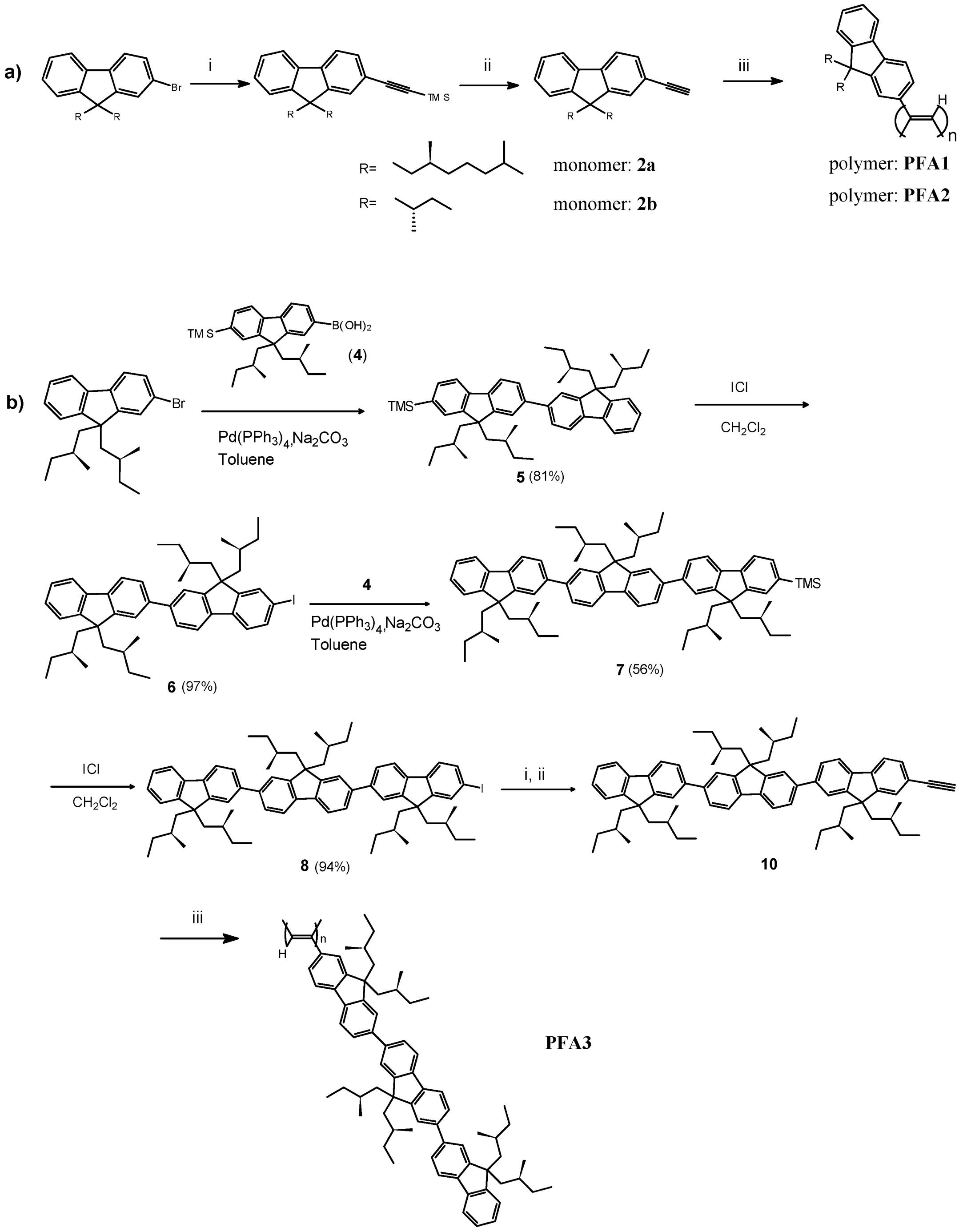
The synthesis of well-defined oligofluorenes monosubstituted onto the aromatic rings is a challenging task that has only recently been addressed.[13,26,28] We have synthesized monomer **10**, as outlined in Scheme 1b, using 2-trimethylsilyl-9,9-[(*S*)-2-methylbutyl]fluoren-7-ylboronic acid (**4**) as building block. The peculiarity of **4** is the presence of a reactive functionality (the boronic acid) and a protecting trimethylsilyl group, which can be converted to a reactive iodide by iododesilylation with ICl. We have used this building block for a step-by-step growth of the oligofluorene chain: the Suzuki coupling of **4** with 2-bromo-9,9-[(*S*)-2-methylbutyl]fluorene followed by reaction with ICl afforded the bifluorene **6**, which was again subjected to Suzuki coupling with **4**; after iododesililation the iodoterfluorene **8** was obtained. As for **2a** and **2b**, the introduction of the terminal acetylene group on the terfluorene moiety was accomplished by palladium-catalyzed Sonogashira coupling of **8** with trimethylsilylacetylene, followed by deprotection with potassium fluoride. The terminal acetylene gives IR stretching frequencies at 3310 and 2106 cm^{-1} and is responsible for a signal at δ 3.14 in the ^{1}H NMR spectrum.

Polymerization Reactions. The acetylenic monomers **2a** and **2b** have been polymerized using [(nbd)-RhCl]$_2$ in THF/Et$_3$N[29] to yield the polymers **PFA1** and **PFA2** (Scheme 1). The catalytic system was chosen in order to warrant a high cis stereoregularity of the polymer backbone.[20] The polymerization of these substrates proceeded smoothly, notwithstanding their bulkiness. After reaction, the products have been isolated by precipitation in methanol and repeatedly washed with ethanol in order to eliminate traces of oligomers and cyclotrimers. The polymers are soluble in dichloromethane, chloroform, and toluene. The reaction conditions and the main features of the obtained materials are reported in Table 1.

Carrying out the polymerization of **10** under the same condition used for **2a** and **2b**, a material insoluble in all common organic solvents was obtained. Using toluene as solvent and carrying out the reaction with a lower monomer/catalyst ratio and higher diluition led to a polymer soluble in chloroform and toluene, although the polydispersity of the obtained material was consequently higher.

The polymerizations were also confirmed by IR spectroscopy. The comparison between the infrared spectra of the monomers and the corresponding polymers **PFA1−3** showed the disappearance of the typical stretching bands of terminal acetylenes at 3310 and 2106 cm^{-1}, as exemplified for **PFA3** in Figure 1. The ^{1}H NMR spectra of **PFA1−3**, carried out in CD$_2$Cl$_2$ or CDCl$_3$, only show broad humps in the region of aromatic protons which may be a consequence of the rigid polyacetylene backbones. This prevents any NMR quan-

Scheme 1. (a) Synthesis and Polymerization of 2a and 2b; (b) Synthesis and Polymerization of 10[a]



[a] *i:* trimethylsilylacetylene, $PdCl_2(PPh_3)_2$, PPh_3, $HNEt_2$ (reflux); *ii*: KF, CH_2Cl_2/CH_3OH (reflux); *iii*: $[Rh(nbd)Cl]_2$.

tification of the backbone cis-stereoregularity. A similar effect was observed in systems bearing OPV as pendant groups.[14]

Thermal and Structural Properties. Thermal analyses of the polymers were performed by DSC and TGA. The relevant data are reported in Table 2.

All the polymers are stable up to 290 °C. This stabilty has been ascribed to the so-called "jacket effect" which consists of the wrapping of the polyacetylene backbones by bulky substituents.[15a] The presence of an exothermic peak, close to the onset of decomposition for **PFA1** and **PFA2**, can be related to a process involving the backbone (e.g., cis to trans or cis-transoidal to cis-cisoidal isomerization) which is the starting step for depolymerization in poly(phenylacetylene).[30] Notably, for **PFA1** an endothermic peak at 170 °C was observed while no such peaks could be detected for **PFA2**. This different thermal behavior could be related to the dimension of the alkyl chains of the two polymers: the C_{10} bulky pendants linked to the polyene backbones in **PFA1** are subject to easier segmental movements, and this may account for the observed transition temperature. No clear DSC transitions were observed for **PFA3**, presumably related to the rigid structure of the polymer. XRD measurements provided an insight into the molecular packing arrangements of the polymers. **PFA1** and **PFA2** showed broad Bragg reflections at high 2θ values (corresponding to layer spacings of 4.60 and 4.46 Å, respectively) and relatively sharper reflections at low 2θ values (corresponding to layer spacings of 19.9 Å for

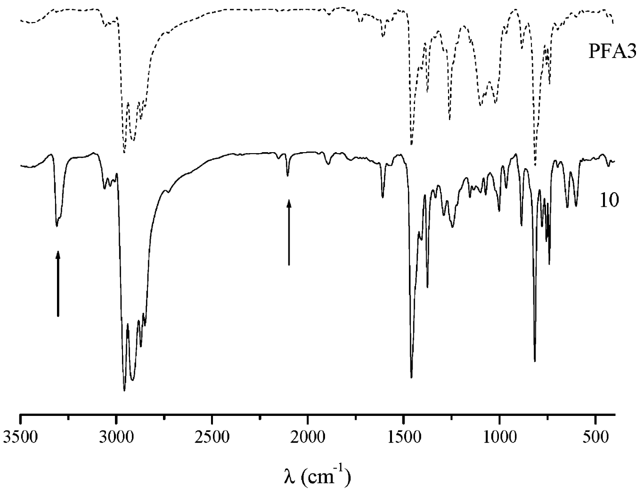


Figure 1. IR spectra (KBr) of **10** and **PFA3**.

Table 2. TGA and DSC Data for the Poly(fluorenylacetylene)s PFA1−3

polymer	endothermic peak (max temp/ enthalpy)	exothermic peak (max temp/ enthalpy)	decomposition (onset temp/ % residue)
PFA1	170 °C/negligible	291 °C/(39 J/g)	290 °C/98.16
PFA2		300 °C/(73 J/g)	300 °C/99.70
PFA3			300 °C/97.57

PFA1 and of 17.7 Å **PFA2**). The reflections at low 2θ values are typically attributed to the interchain distances between polyenic backbones.[31] The smaller alkyl chain in **PFA2** seems to favor a closer packing and therefore a shorter interchain distance with respect to **PFA1**. The peaks at 4.60 and 4.46 Å are due to the reticular planes identified by the fluorene systems parallel to each other. In Figure 2 are shown the X-ray diffraction pattern and the probable supersecondary structure of **PFA1** and **PFA2**, exemplified for the former. **PFA3** is completely amorphous because of the bulkiness of the pendant group, which prevents a regular tridimensional organization.

Optical and Photoluminescence Properties. The UV−vis absorption spectra of **PFA1** and **PFA2** in solution ($CHCl_3$) and of **PFA3** in solution and as thin film (obtained by drop-casting from 1 mg/mL chloroform solution) are shown in Figure 3, together with a comparison with the spectra of the corresponding monomers in solution. **PFA1** and **PFA2** exhibit very similar absorption spectra due to the similarity of their primary structure, with a maximum at 320 nm and a shoulder placed at 290 nm. These bands are due to $\pi-\pi^*$ transitions of fluorene units, as confirmed by the comparison with the absorption spectra of the monomers **2a** and **2b**. The peaks at 458 and 445 nm respectively for **PFA1** and **PFA2** are ascribable to $\pi-\pi^*$ transitions of the polyene backbones. These bands are red-shifted with respect to analogous polyenes [for instance, the corresponding absorption band in poly(phenylacetylene) falls at ca. 400 nm], thus pointing out a higher conjugation length of the polyene backbones. This planarization is presumably a consequence of the twisting of the fluorene groups orthogonally with respect to the plane of the backbone, caused by steric repulsion between the bulky pendant groups as observed in similar systems.[32] This spatial arrangement implies a poor conjugation between polyenic backbone and fluorene pendant groups and would account for the presence of two independent chromophores in both **PFA1** and **PFA2**. The 13 nm red shift of the backbone absorption band of **PFA1** respect to **PFA2** could be ascribed to a more planar conformation of the former.

As shown in Figure 3b, the absorption spectrum of **10** evidences a maximum at 353 nm, corresponding to the $\pi-\pi^*$ transition of the terfluorene unit. As a consequence of the much higher extinction coefficient of the terfluorene compared to that of the polyacetylene backbone, the contribution of the $\pi-\pi^*$ transition of the backbone to the absorption spectrum of **PFA3** is minor. The polymer shows an absorption band slightly red-shifted with respect to the monomer, together with a tail at longer wavelengths attributable to the $\pi-\pi^*$ transition of the polyene backbone. In the solid state the absorption curve of **PFA3** consists of a broad band centered at 358 nm.

Photoluminescence (PL) spectra were recorded for the monomers **2a** and **2b** and for the relevant polymers **PFA1** and **PFA2** (λ_{ex} = 290 nm); the comparison is depicted in Figure 4a. The monomer spectra show the typical vibronic fine structure of the monofluorene system with two maxima at 320 and 336 nm. This structure is not observable in both **PFA1** and **PFA2** spectra which show only a maximum at 337 nm. No signal was detected by recording the PL spectrum of **PFA1** and **PFA2** at λ_{ex} = 450 nm, thus confirming the scarce emitting ability of the backbone of monosubstituted polyarylacetylenes.[19]

The fluorescence spectra of **10** and of **PFA3** (λ_{ex} = 350 nm) are reported in Figure 4b. **10** shows the typical vibronic structure of oligofluorenes with maxima at 400, 422, and 447 nm. The λ_{max} for **PFA3** in solution are unchanghed respect to the monomer, except for their relative intensity, which is reversed (the absolute maximum is placed at 425 nm). The absence of a red shift in the emission of **PFA3** with respect to the monomer is a hint for the absence of interactions between the luminophores in the macromolecule. In the solid state the emission band falling in the violet-blue region (λ_{max} = 430 nm) is characterized by the loss of the vibronic fine structure.

Chiroptical Properties. The chiral centers on the side chains at the C-9 position in the monomers can be used for probing the helical arrangement of the functionalized polyene backbones. In fact, if an excess in one of the screw senses of the helix is induced, a Cotton effect can be observed in the circular dichroism (CD) spectra of the macromolecules.[33] CD spectra of **PFA1** and **PFA2** (Figure 5) in chloroform at room temperature showed a bisignated Cotton effect in the region of the polyene backbone absorption.

In the case of **PFA2**, this Cotton effect is more pronounced; the difference in the intensity of the CD response between the two polymers may be due to the closeness to the polyene backbone of the chiral center as well as to the steric hindrance of the pendant groups. The considerable lower Cotton effect observed for **PFA1** can in fact be ascribed to the influence of the (*S*)-3,7-dimethyloctyl chains which, as confirmed by the UV−vis observation, may be held responsible for a stabilization of the planar polyene conformation.[34] Another interesting aspect which stems from the comparison between the CD measurements is the opposite sign of the dominant chiroptical properties of the two polymers. This phenomenon is a consequence of the opposite screw sense of the two helices induced by the different conformations of the alkyl chains, as confirmed by the

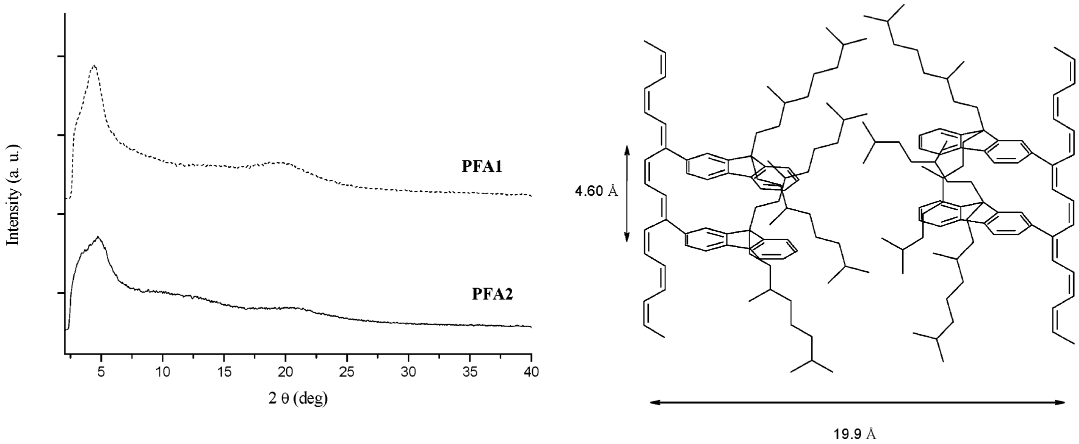


Figure 2. X-ray diffraction of **PFA1** and **PFA2** and proposed bilayer packing arrangement of **PFA1**.

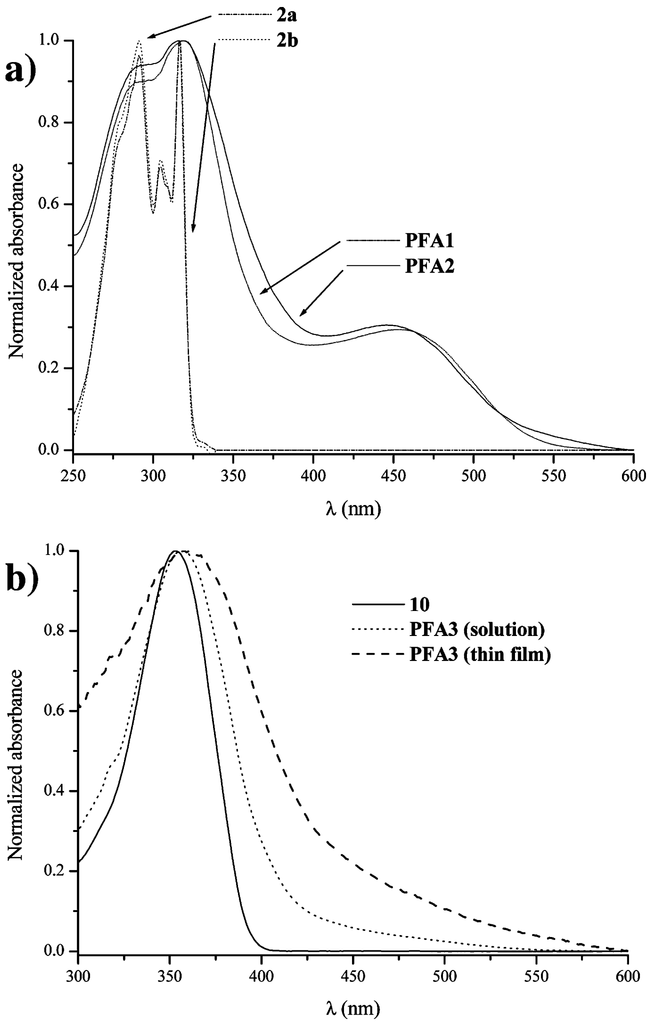


Figure 3. (a) UV−vis absorption spectra of **2a**, **2b**, **PFA1**, and **PFA2** in $CHCl_3$. (b) Comparison of the UV−vis absorption spectrum of **10** with that of **PFA3** in solution and as thin film (thickness ca. 1 μm). [**2a**] = 1.8 × 10^{-5} M, [**2b**] = 1.8 × 10^{-5} M, [**PFA1**] = 3.2 × 10^{-5} M, [**PFA2**] = 2.3 × 10^{-5} M, [**10**] = 0.9 × 10^{-5} M, [**PFA3**] = 1.2 × 10^{-5} M (on the basis of the repeat unit in the case of polymers).

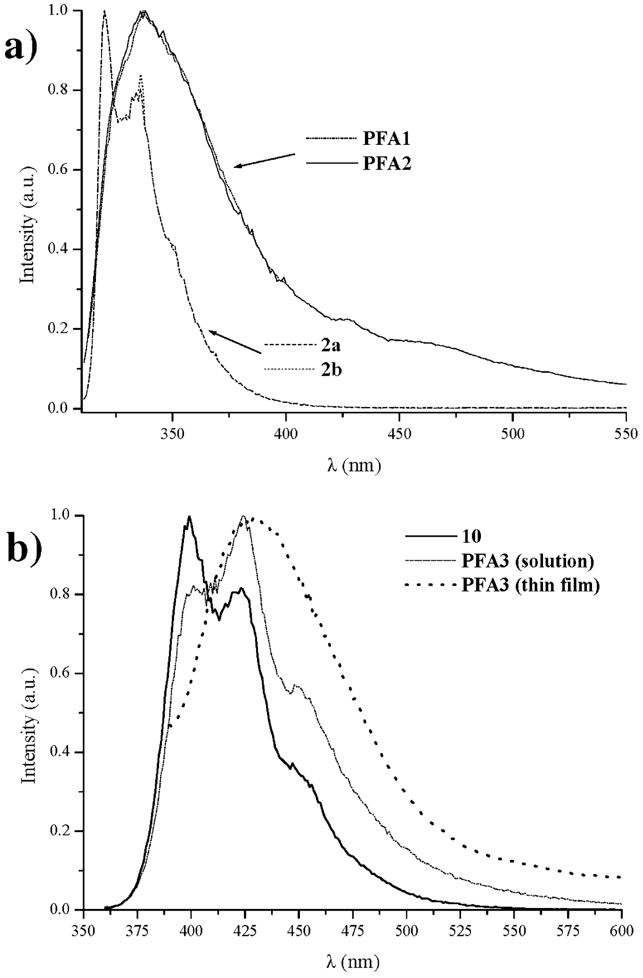


Figure 4. (a) PL spectra of **2a**, **2b**, **PFA1**, and **PFA2** in $CHCl_3$. (b) Comparison of the PL spectrum of **10** with that of **PFA3** in solution and as thin film (thickness ca. 1 μm). The solution concentrations were adjusted in order to exhibit an absorbance of 0.1.

fact that a quite similar effect was observed and rationalized for analogous polyfluorenes.[35] Although **10** and **PFA3** were functionalized with the (*S*)-2-methylbutyl groups (which has warranted the good CD response observed for **PFA2**), these compounds showed no chiroptical properties either in solution or in solid state. A possible reason for the **PFA3** behavior might be either the considerable dimension of the pendant group, which destabilizes any helical secondary structure or the absence of induction of a preferential screw sense on the polyenic backbone of the macromolecule.

Conclusions

The first polyacetylenes functionalized with fluorene moieties as pendant groups were synthesized and characterized. Monofluorene systems bearing (*S*)-3,7-

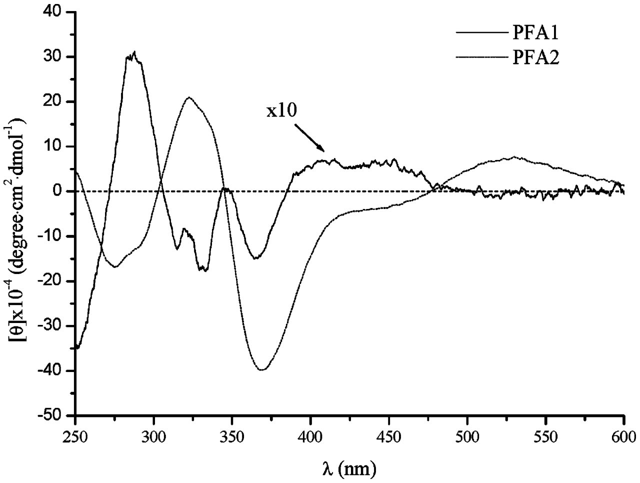


Figure 5. CD spectra of **PFA1** and **PFA2** in $CHCl_3$. [**PFA1**] = 1.4×10^{-5} M, [**PFA2**] = 6.2×10^{-5} M (on the basis of the repeat unit).

dimethyloctyl and (*S*)-2-methylbutyl chains have been functionalized with a terminal acetylene and polymerized. For both polymers (i) DSC-TGA measurements indicate good thermal stability and a rigid polyene core; (ii) XRD measurements point out a bilayer arrangement; (iii) UV−vis and photoluminescence properties in $CHCl_3$ solution support the hypothesis that the polyene backbone does not interact with the fluorene emitters preserving the good optical properties of the latter; and (iv) circular dichroism investigations evidence a helical conformation; moreover, the two different chiral chains induce opposite signs in the relevant Cotton effects. As an extension of the procedure, a synthetic route was devised to insert a terminal acetylene onto a chiral C_5-functionalized terfluorene moiety. The corresponding polymer confirmed the findings observed for the model systems. In particular, a high thermal stability of the polymer was evidenced by DSC and TGA methods. UV−vis features of monomer and polymer are those typical for a molecularly dissolved terfluorene systems. The emitting properties of a drop-cast film of the terfluorene-based polymer follow those found in solution, thus confirming that anchoring an oligofluorene luminophore as pendant group of a polyacetylene represents an efficient method for preventing aggregate formation in the solid state.

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