

Synthesis and optical properties of (thienylene)–[1,6-dithienylhexa-1,3,5-trienylene] copolymers

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Two [thiophene–1,6-dithienylhexa-1,3,5-triene] copolymers were prepared by a palladium catalysed coupling reaction of a dibromothiophene derivative and a bis(tributylstannyl) derivative of a 1,6-dithienylhexa-1,3,5-triene unit. The electrochromism and the photoluminescence properties of the highly conjugated polymers were studied. In the solid state the polymers have strong photoluminescence bands at 2.0 eV for **9** and 1.95 eV for **8**. Polymer **8** seems particularly promising for use as a red-light emitting diode, and the two polymers **8** and **9** exhibit red–pale blue electrochromism that makes them suitable for fabricating new devices.

Conjugated organic oligomers and polymers are attractive materials since a wide range of optical properties can result from variations in their molecular structure. The tuning of optical and electro-optical properties is of interest to elaborate electrochromic or electroluminescent devices.¹ Among these materials, poly(*para*-phenylene vinylene) and its derivatives have been extensively used for blue–green electroluminescent devices but red light emitting materials are more scarce. For electrochromic devices, conjugated polymers, especially those based on polythiophenes^{2,3} such as poly(3,4-ethylenedioxythiophene),⁴ appeared particularly interesting because of their transparency in the doped state. The tailoring of electrochromic properties is currently obtained upon blending at least two polymers exhibiting different electrochromic properties.⁵

Our current interest in polymers with tunable electrooptical properties led us to study the synthesis of well-defined copolymers. We recently reported the synthesis of highly conjugated thiophene–alkylthiophene⁶ and [thienylene–*p*-(2,5-dialkoxy)phenylene]⁷ copolymers with electroluminescent and electrochromic properties. The photophysics of α,ω -diphenyl- and -dithienyl oligomeric polyenes have been extensively studied by theoretical and experimental approaches.^{8,9} Poly(*p*-phenylenehexa-1,3,5-trienylene) with a small number of repeat units presented electronic spectroscopic data at relatively high energy.¹⁰ After being doped, such molecular structures offer distinct color contrasts corresponding to polaronic radical cations and bipolaronic dication species.^{11,12} These molecular entities are presently sought after for their optical power limiting properties¹² and their incorporation in the backbone of an organic conjugated polymer is of great interest to produce materials with optical properties.

Here, we report the synthesis of two well-defined conjugated copolymers containing thienylene and 1,6-dithienylhexatriene chain units. The electrochromism and the photoluminescence of the prepared copolymers are discussed.

Results and discussion

1. Polymers synthesis

The synthesis of the two polymers was achieved using the Stille coupling reaction between a 2,5-dibromothiophenyl substrate and a bis(tributylstannyl) aromatic derivative in the presence of

Pd(o) as the catalyst. It has already proved to be an efficient route to regioregular poly(3-alkylthiophene)^{6,13,14} and to alternating thienylene–1,4-dialkoxyphenylene copolymers.

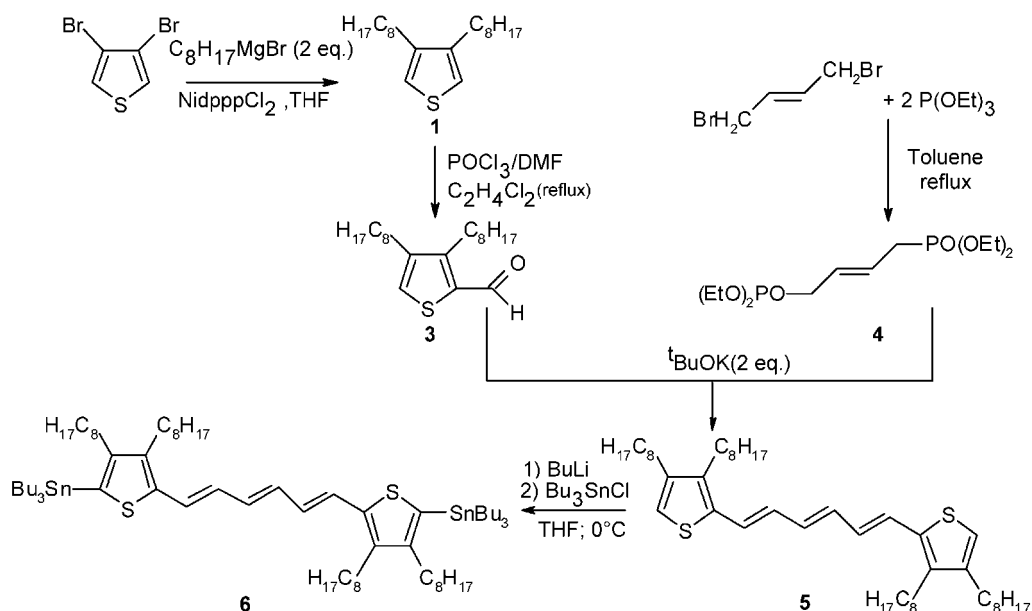
The synthesis of **5** began with the 3,4-alkylation of thiophene in dry THF by reaction of the octylmagnesium bromide with 3,4-dibromothiophene in the presence of a catalytic amount of 1,3-bis(diphenylphosphino)propanenickel(II) chloride. 3,4-Dioctylthiophene (**1**) was then formylated with DMF in the presence of phosphorus oxychloride in 1,2-dichloroethane as the solvent. The 3,4-dioctylthiophene-2-carboxaldehyde (**3**) obtained reacted with tetraethyl (*E*)-but-2-ene-1,4-diylidiphosphonate (**4**) in the presence of two equivalents of *t*BuOK in THF to give **5** according to a Wittig–Horner reaction. Compound **5** was treated at low temperature with butyllithium in THF and distannylated with Bu₃SnCl (Scheme 1).

The polymers **8** and **9** were synthesised by a polycondensation reaction using 2,5-dibromothiophene and 2,5-dibromo-3-octylthiophene (**7**) respectively with an equimolar ratio of the bis(tributylstannyl) derivative **6**. This reaction gave THF or CHCl₃ soluble conjugated regular copolymers containing alternating thienylene and (*E,E,E*)-1,6-bis(3',4'-dioctyl-2'-thienyl)hexa-1,3,5-triene (Scheme 2).

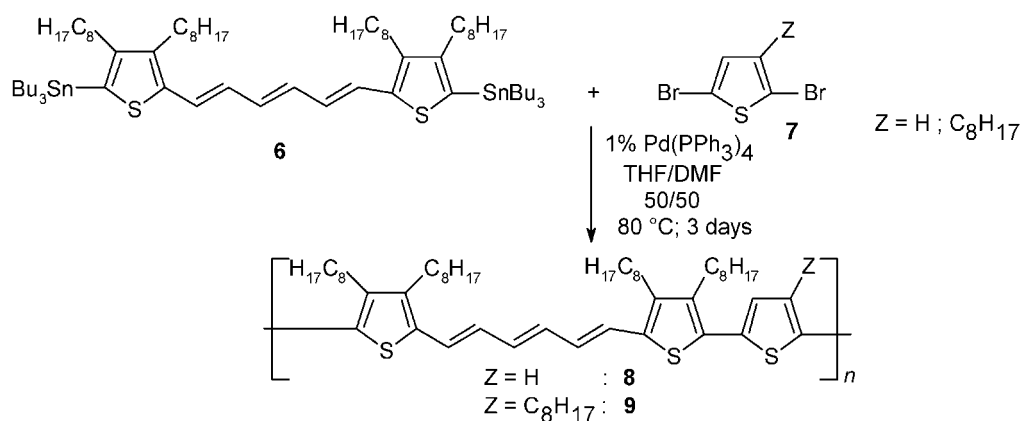
The spectroscopic data are consistent with the structure of **8** and **9** described in Scheme 1. The EDAX analysis of the two isolated solid materials revealed only traces of Sn and Br and the absence of Pd. The ¹H NMR spectra of **8** and **9** showed two groups of signals at 7.1 ppm (thienylene protons) and at 6.70 ppm (vinylene protons). It also showed at higher field signals corresponding to the octyl substituents of the thienyl rings. The polymers were soluble in organic solvents (THF, CHCl₃) and were analysed using gel permeation chromatography (GPC) on styragel columns calibrated with polystyrene standards using THF as eluent. Average molecular weights *M*_w in the range 3000–4000 and polydispersities *M*_w/*M*_n in the range 1.4–1.8 were observed (Table 1). It indicates an average degree of polymerisation (DP_n) of only 4 or 5 of the chain unit containing 18 conjugated carbon atoms.

2. Optical properties

The UV–Vis and the fluorescence spectra were recorded from thin films on glass (Table 1). As with poly(*p*-phenylenehexa-1,3,5-trienylene),¹⁰ the absorption of compounds **8** and **9** is at



Scheme 1 Synthesis of *(E,E,E)*-1,6-bis(2'-thienyl-3',4'-dioctyl-5'-tributylstannyl)hexa-1,3,5-triene (**6**).



Scheme 2 Synthesis of copolymers **8** and **9**.

high energy in the range 450–466 nm. It is consistent with low conjugation length probably due to the high flexibility of the hexatrienyl system.

2.1. Electrochromic properties

Films of **8** and of **9** were formed on a platinum electrode from a 10^{-3} M solution in CHCl_3 and the deposits were studied by cyclic voltammetry. The voltammograms were recorded between -2 and $+1$ V (vs. SCE). Each polymer showed an oxidation peak and a corresponding reduction one (Table 2 and Fig. 1). Polymers **8** and **9** appeared easier to oxidize than polythiophene.¹⁵ Oxidation of **9** occurred at a higher potential value than the oxidation of **8**. This is indicative of a lower

conjugation in **9** owing to the presence of the alkyl substituent. The alkyl substituents induce some steric hindrance and cause defects in the planar arrangement of the conjugated segments. Related observations were made for head to head coupling which leads to conjugation defects in polythiophene whereas regioregular poly(alkylbithiophene)s exhibit extended conjugation.¹⁴ The absorption UV–Vis spectrum of **8** ($\lambda_{\text{max}} = 466$ nm), with a higher wavelength value than **9** ($\lambda_{\text{max}} = 450$ nm), is consistent with a lower conjugation in **9** compared with **8**.

Polymers **8** and **9** exhibited a red–pale blue electrochromism, associated with the redox behavior. The electrochromic phenomenon was studied using a spectroelectrochemical cell made in our laboratory (Fig. 2). It is a standard UV–Vis spectroscopy cell in which a 7×25 mm indium tin oxide (ITO) glass plate as working electrode, a flexible Pt wire as the counter electrode and an Ag wire as the reference electrode are placed. A curved lead plate is pinched on to the top of the ITO plate to improve the electrical contact. To avoid any contact

Table 1 Selected data for polymers **8** and **9**

Polymers	M_w^a	M_w/M_n	DPn ^b	Absorption $\lambda_{\text{max}}/\text{nm}$ films on glass	Emission $\lambda_{\text{max}}/\text{nm}$ films on glass
8	3019	1.8	3.9	466	636
9	4187	1.4	4.7	450	620

^aDetermined by GPC using polystyrene standards. ^bDegree of polymerisation.

Table 2 Voltamperometry data of polymers **8** and **9**

Polymers	$E_{\text{pox}}(\text{vs. SCE})/\text{V}$	$E_{\text{pred}}(\text{vs. SCE})/\text{V}$
8	0.77	0.74
9	0.93	0.81

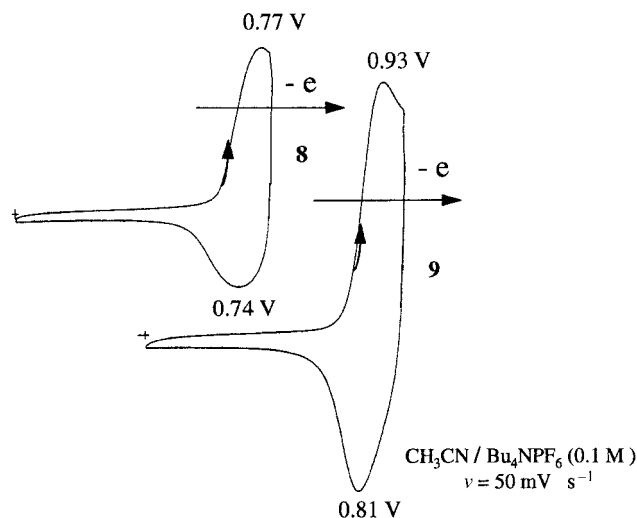


Fig. 1 Cyclic voltamperometry of polymers **8** and **9**.

between electrodes, two teflon blocks are placed at the bottom and at the top of the cell. The sample is deposited on the ITO glass support by slow evaporation of a 10^{-4} M solution so that it is crossed by the optical beam of the UV-Vis spectrophotometer. The cell is filled with an electrolytic solution and placed in the sample compartment of the spectrophotometer. The three electrodes are then connected to a potentiostat (Fig. 2).

Films of **8** and **9** were deposited from (10^{-4} M) solutions of polymer in CHCl_3 , on an ITO glass support. The absorption spectra were recorded for the films of polymer immersed in a (0.1 M) solution of Bu_4NPF_6 as the supporting electrolyte in CH_3CN . The applied potential varied between 0 and 1 V. The changes in the absorption spectra as a function of the applied potential are shown in Fig. 3 for **8** and in Fig. 4 for **9**. For the two polymers, in the neutral form, the absorption spectra showed a single band associated with an interband transition, respectively at $\lambda = 466$ nm for **8** and $\lambda = 450$ nm for **9**. Upon oxidation, the absorption maximum, associated with the appearance of polaronic and bipolaronic states, shifts to higher wavelengths. The position of the absorption band of the polymeric species could be correlated to the absorption of the radical cation in the near infrared domain of the di-2'-thienylhexa-1,3,5-triene unit.¹² For each polymer studied (**8** and **9**), there is an isosbestic point in Fig. 3 and in Fig. 4 respectively, revealing that only two absorption bands are involved. It is interesting to note that **8** and **9** have optical properties tunable between one quasi transparent and one opaque state. The electrochromic behavior appeared similar to poly(3,4-ethylenedioxythiophene) (PEDOT).⁴ The low absorp-

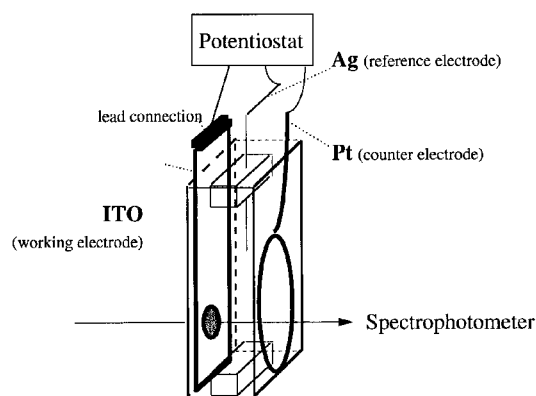


Fig. 2 Electrochromic device.

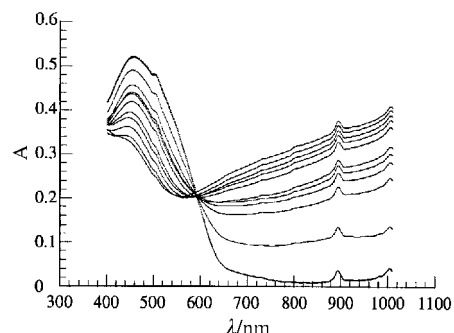


Fig. 3 Variation of the absorption spectrum of a film of **8** on an ITO support as a function of the applied potential in the range 0–1 V.

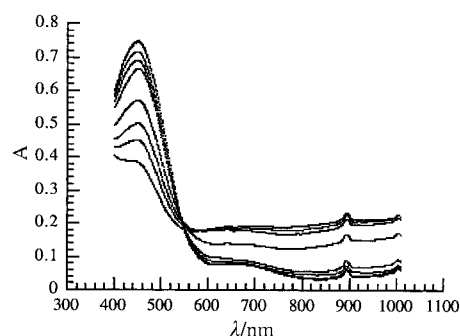


Fig. 4 Variation of the absorption spectrum of a film of **9** on an ITO support as a function of the applied potential in the range 0–1 V.

tion of these polymers in the visible range in the oxidized state makes them interesting for various uses,⁷ for example, as smart windows and energy saving windows.¹⁶

2.2. Photoluminescence study

Emission properties of **8** and **9** have been studied in order to evaluate their ability as materials suitable for electroluminescent devices. The room temperature photoluminescence (PL) bands recorded on thin films of **8** and **9** are displayed in Fig. 5a. The profiles of these bands are similar. The maximum of the PL band occurs at 2 eV ($\lambda = 620$ nm) for **9** and at 1.95 eV ($\lambda = 636$ nm) for **8**. A displacement to low energy with the increase of the conjugation length was observed in thiophene-based regioregular polymers.¹⁴ By analogy this shift is attributed to a higher conjugation, and thus to a gap, smaller in polymer **8** than in polymer **9**. The temperature dependence of the PL band does not reveal significant changes (Fig. 5b).

Red-emitting diodes are presently sought after and it is worth noting that **8** is a red-emitting polymer ($\lambda = 636$ nm). Moreover, in the range of cathodic potentials, a reduction wave was observed only for **8** at -1.7 V (vs. SCE) and revealed a high electron affinity of **8**. The observed value is compatible with the extraction potential of magnesium ($E^\circ(\text{Mg}^{2+}/\text{Mg}) = -2\text{V}$) as electrode material. The polymer **8** may therefore be of interest to fabricate electroluminescent diodes. The realisation of light emitting diodes with **8** is now in progress.

Experimental

Solvents were dried by distillation over phosphorus pentoxide (CHCl_3), sodium benzophenone ketyl (toluene, THF, ether) and CaH_2 (hexane, DMF). 3,4-Dibromothiophene, 3-bromothiophene, 1-bromooctane, 2,5-dibromothiophene and tributyltin chloride (Aldrich) were used without further purification. Ni(dppp)Cl_2 and *n*-butyllithium in 2.5 M solution in hexanes were purchased from Aldrich.

¹H NMR spectra were recorded in CDCl_3 at 200 MHz with a

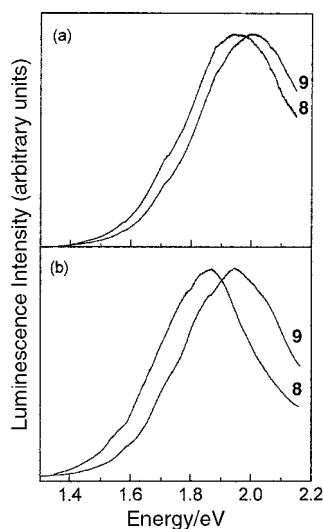


Fig. 5 Photoluminescence of polymers **8** and **9** recorded at: a) room temperature; b) 10 K.

Bruker AC 200 spectrometer, using residual CHCl_3 ($\delta = 7.27$ ppm) as the internal standard. ^{13}C NMR spectra were obtained at 50.32 MHz with a Bruker AC 200 using CDCl_3 ($\delta = 77.70$ ppm) as the internal standard. IR spectra were recorded with a Perkin-Elmer 1000 spectrometer. Melting points were measured with an Electrothermal 9100 apparatus. Absorption spectra were recorded on a MC² Safas spectrometer and emission spectra on a SLM-Aminco MC 200 spectrometer. Fluorescence quantum yields were measured by the standard procedure.¹⁷ GPC measurements were carried out on a Waters chromatograph equipped with HR₂ and HR₃ Styragel columns. Mass spectra (FAB) were obtained using a JEOL JMS-DX 300 apparatus. Cyclic voltammetry was carried out on an EGG potentiostat connected to a Kipp & Zonen tracer. Electrochromism measurements were made from a three electrode (ITO, Pt, Ag) spectroelectrochemical cell connected to an EGG 362 potentiostat. EDAX measurements were carried out using a Cambridge 360-stereoscan with an EDS-Link AN 10000 attachment. Raman spectra were recorded using a Jobin-Yvon T64000 spectrometer equipped with a liquid nitrogen cooled CCD detector. The measurements were performed in the back scattering configuration using an Ar-ion laser (Spectra Physics 2000) with 514.5 nm exciting radiation. All spectra were realized under vacuum to avoid degradation of the sample. The samples were maintained in a cryostat (Air Liquide) where the temperature could be varied between 5 and 300 K. To minimize the local heating the power density was kept below 5 mW mm^{-2} .

3,4-Dioctylthiophene (1)

Into a three-necked flask equipped with a magnetic stirrer, dropping funnel and a condenser 7.1 g (293 mmol) of magnesium powder and 5 mL of dried THF were introduced under a nitrogen atmosphere. A few drops of pure 1-bromooctane (43.75 mL, 226 mmol) were added from the funnel to the medium. As soon as the reaction started the remaining 1-bromooctane was diluted in 150 mL of dry THF and added dropwise. After complete addition, the medium was heated and refluxed for 3 hours.

The octylmagnesium bromide was added at 0 °C to a solution of 23.58 g of 3,4-dibromothiophene (97.4 mmol) and 0.525 g of 1,3-bis(diphenylphosphino)propanenickel(II) chloride in 100 mL of dry THF. After the addition was completed, the mixture was refluxed for four hours at least, then cooled to room temperature. Magnesium salts were precipitated with a large excess of hexane. After filtration, the solvent was

evaporated and the obtained oil was quickly eluted on a 5 cm long silica gel column with hexane. The solvent was removed and **1** was isolated in 64% yield by distillation *in vacuo*. Bp 145 °C/0.4 mmHg; ^1H NMR (CDCl_3) δ_{H} ppm: 0.95 (6 H, t, CH_3), 1.34 (20 H, m, 5 CH_2), 1.67 (4 H, m, βCH_2), 2.55 (4 H, t, αCH_2), 6.92 (2 H, s, $\text{H}_{\text{thienyl}}$); ^{13}C NMR (CDCl_3) δ_{C} ppm: 14.16 (CH_3), 22.76, 28.89, 29.37, 29.58, 29.7, 29.75, 31.9 (CH_2 , alkyl chain), 119.9 ($\text{C}_{\text{thienyl}}$ C₂, C₃), 142.1 ($\text{C}_{\text{thienyl}}$ C₃, C₄); MS: m/z : 309 ($\text{M}^+ + 1$) (100%). Found: C, 77.80; H, 11.76. $\text{C}_{20}\text{H}_{36}\text{S}$ requires C, 77.85; H, 11.76%.

3-Octylthiophene (2)

This compound was prepared according to the literature.¹⁸

3,4-Dioctylthiophene-2-carboxaldehyde (3)

In a Schlenk tube under a nitrogen atmosphere 1,2-dichloroethane (40 mL), **1** (7.07 g, 23 mmol) and DMF (2.1 g, 28.7 mmol) were successively introduced. The medium was cooled to 0 °C and 4.4 g (28.7 mmol) of oxyphosphorus chloride were added dropwise. After complete addition, the medium was heated and refluxed for three hours. It was then cooled to room temperature, poured into an aqueous acidic (HCl 10%) solution and stirred for one hour. The organic phase was extracted with dichloromethane, washed several times with an aqueous sodium hydrogen carbonate solution, and dried over magnesium sulfate. The solvent was evaporated and the crude product was distilled under reduced pressure. Yield 97%, bp 165 °C/0.3 mmHg; ^1H NMR (CDCl_3) δ_{H} ppm: 0.88 (6 H, m CH_3), 1.28 (20 H, m, 5 CH_2), 1.55 (4 H, m, βCH_2), 2.53 (2 H, t, αCH_2), 2.87 (2 H, t, αCH_2), 7.33 (1 H, s, $\text{H}_{\text{thienyl}}$), 10.0 (1H, s, H_{ald}); ^{13}C NMR (CDCl_3) δ_{C} ppm: 14.09 (CH_3), 22.65, 22.66, 27.03, 28.26, 29.19, 29.24, 29.32, 29.42, 29.47, 29.63, 29.71, 29.80, 31.84, 31.36, 31.93, 130.23 ($\text{C}_{\text{thienyl}}$, C₃), 138.18 ($\text{C}_{\text{thienyl}}$, C₄), 144.39 ($\text{C}_{\text{thienyl}}$, C₃), 151.50 ($\text{C}_{\text{thienyl}}$, C₂), 182.60 (C_{ald}); HRMS (FAB⁺): calculated for $\text{C}_{21}\text{H}_{37}\text{OS}$: m/z 337.2565; observed 337.2608. Found: C, 74.84; H, 10.63. $\text{C}_{21}\text{H}_{36}\text{OS}$ requires C, 74.94; H, 10.78%.

Tetraethyl (E)-but-2-ene-1,4-diylidiphosphonate (4)

This compound was prepared according to the literature.¹⁹

(E,E,E)-1,6-Bis(3',4'-dioctyl-2'-thienyl)hexa-1,3,5-triene (5)

Into a three-necked flask equipped with a condenser and a dropping funnel **4** (3.34 g, 8.66 mmol) and **3** (6.45 g, 19.08 mmol) in 100 mL of dry THF were introduced under nitrogen. From the funnel was added dropwise a solution of 2.62 g (23.4 mmol) of potassium *tert*-butoxide in 80 mL of dry THF. The mixture became first yellow then black. After complete addition the medium was stirred at room temperature for 12 hours. The solution was then poured into 250 mL of distilled water at 0 °C and stirred for one hour. A solid phase appeared, and was filtered and dissolved in dichloromethane. This organic phase was dried over MgSO_4 , filtered and concentrated *in vacuo*. The obtained oil was chromatographed over a silica gel column using hexane-ethyl acetate (95:5) mixture as the eluent. A yellow powder was obtained in 85% yield after the solvent was removed. Mp 47 °C; ^1H NMR (CDCl_3) δ_{H} ppm: 0.89 (12 H, t), 1.28 (40 H, m), 2.50 (8 H, m), 6.44 (2 H, m), 6.68 (2 H, m), 6.74 (2 H, s); ^{13}C NMR (CDCl_3) δ_{C} ppm: 14.15, 22.72, 26.98, 29.04, 29.32, 29.46, 29.53, 29.63, 29.73, 29.80, 31.08, 31.94, 118.36, 124.22, 128.07, 132.72, 137.14, 140.11. Absorption: λ_{max} (10^{-4} M) CHCl_3 solution) 400 nm. MS: m/z : 692 ($\text{M}^+ + 1$) (100%). Found: C, 79.55; H, 10.63. $\text{C}_{46}\text{H}_{76}\text{S}_2$ requires C, 79.79; H, 11.05%.

(*E,E,E*)-1,6-Bis(3',4'-dioctyl-5'-tributylstannyl-2'-thienyl)hexa-1,3,5-triene (6)

Under a nitrogen atmosphere, **5** (2 g, 2.89 mmol) and dry THF (50 mL) were introduced into a Schlenk tube. The medium was cooled to -80°C and 2.54 mL (6.34 mmol) of a solution of *n*-butyllithium in hexane (2.5 M) were added. After the reaction mixture was stirred at -80°C for one hour, Bu_3SnCl (2.07 g, 6.34 mmol) was added dropwise and the solution was left under stirring for eight hours. After hydrolysis, the organic phase was extracted three times with 50 mL of ether, dried with magnesium sulfate, filtered and concentrated *in vacuo*. The crude oil obtained in 95% yield is used without purification. ^1H NMR (CDCl_3) δ_{H} ppm: 0.91 (30 H, m), 1.37 (84 H, m), 2.50 (8 H, m), 6.45 (2 H, m), 6.66 (4 H, d), ^{13}C NMR (CDCl_3) δ_{C} ppm: 28 signals between 32.65 and 10.95, 123.99, 128.20, 131.25, 132.69, 140.98, 142.83, 150.95. Absorption: λ_{max} (10^{-4} M) CHCl_3 solution) 418 nm.

2,5-Dibromo-3-octylthiophene (7)

To a solution of 5.36 g (27.4 mmol) **2** in 40 mL of CHCl_3 were added dropwise 3.07 g (60.2 mmol) of bromine in 30 mL of CHCl_3 . The reaction mixture became immediately red and after complete addition the reaction mixture was stirred at room temperature for ten hours. The medium was then washed first with a 20% potassium hydroxide solution until the red colour disappeared. The organic phase was dried over magnesium sulfate, filtered and concentrated. The product was obtained in 76% yield as a colorless oil after distillation under reduced pressure. The analytical data agreed with those reported in the literature.²⁰ Bp $130^{\circ}\text{C}/0.3\text{ mmHg}$. ^1H NMR (CDCl_3) δ_{H} ppm: 0.92 (3 H, t, CH_3), 1.31 (10 H, m, 5 CH_2), 2.49 (2 H, t, CH_2), 6.75 (1 H, s, $\text{H}_{\text{thienyl}}$); ^{13}C NMR (CDCl_3) δ_{C} ppm: 14.23, 22.78, 29.23, 29.32, 29.44, 29.57, 29.67, 31.97, 108.02, 110.41, 130.95, 142.97.

Copolymers

Copolymers **8** and **9** were synthesised according to the same experimental procedure. The only change that leads to copolymer **8** or **9** concerns the dibromo compound used in the coupling reaction.

Copolymer 8

In a Schlenk tube equipped with a condenser, $\text{Pd}(\text{PPh}_3)_4$ (0.0115 g, 10^{-5} mol) in 10 mL of a THF–DMF (50:50) mixture was dissolved under a nitrogen atmosphere and at room temperature. Compound **7** (0.001 mol, 0.402 g) and 0.001 mol (0.242 g) of 2,5-dibromothiophene were introduced by a syringe. The reaction mixture was stirred at 80°C during three days. Heating was then stopped and a red precipitate formed upon the addition of acetone. The powder was filtered, washed with acetone and dried *in vacuo* to give 0.697 g of **8** (Yield 90%). ^1H NMR (CDCl_3) δ_{H} ppm: 0.90 (12 H, t, 4 CH_3), 1.33 (48 H, m, 24 CH_2), 2.63 (8 H, t, 4 CH_2), 6.65 (6 H, m, CH_{vinyl}), 7.13 (2 H, d, $\text{CH}_{\text{thienyl}}$); ν_{max} (KBr)/ cm^{-1} : 2924, 2360, 1608, 1465, 1375, 984, 790. Found: C, 69.95; H, 8.78%. EDAX analysis: Sn/S: 0.1; Br/S: 0.08. Absorption: λ_{max} (film on glass) 466 nm. Emission: λ_{max} (film on glass) 636 nm.

Copolymer 9

For the preparation of copolymer **9**, **7** (0.001 mol, 0.402 g) and **6** (0.001 mol, 0.354 g) were reacted (Yield 90%) (0.797 g). (CDCl_3) δ_{H} ppm: 0.92 (15 H, t, 5 CH_3), 1.36 (60 H, m, 30 CH_2), 2.65 (10 H, t, 5 CH_2), 6.70 (6 H, m, CH_{vinyl}), 7.15 (1 H, s, $\text{CH}_{\text{thienyl}}$); ν_{max} (KBr)/ cm^{-1} : 2925, 2854, 1609, 1465, 1377, 985, 873, 722. Found: C, 71.58; H, 9.18%. EDAX analysis: Sn/S: 0.1; Br/S: 0.13. Absorption: λ_{max} (film on glass) 450 nm. Emission: λ_{max} (film on glass) 620 nm.

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