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Synthesis and ionochromic properties of chelating conjugated polymers

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Two types of conjugated copolymers functionalized by chelating subunits were prepared using the palladium catalysed coupling reaction of a dihalogenated substrate containing a coordinating unit and a bis(tributylstannyl) conjugated reagent. The ionochromic properties of the polymers containing crown ethers or bipyridine were studied.

Poly(*p*-phenylene-vinylene)s are of great interest for their photophysics, charge transport and optoelectronic properties.[1] Additionally, it has been shown more recently that some (2,2′-bipyridyl-*p*-phenylene-vinylene) based polymers exhibit ionochromic properties in the presence of a wide variety of transition metal ions.[2] Moreover, their optoelectronic properties can be controlled by protonation–deprotonation processes.[3] Related chemoresponsive polymers are of interest for the design of selective sensory materials.

Substituted polythiophenes with side chains containing crown ether[4] or calix[4]arene[5] also exhibit selective ionochromism. Our current interest in the controlled synthesis of thiophene-phenylene and thiophene vinylene copolymers[6] has led us to study the synthesis of polythiophene-phenylene copolymers containing complexing units in the backbone of the polymer. The optical properties of these copolymers where the complexing unit is part of the polymer backbone are expected to be strongly dependent on the ion.

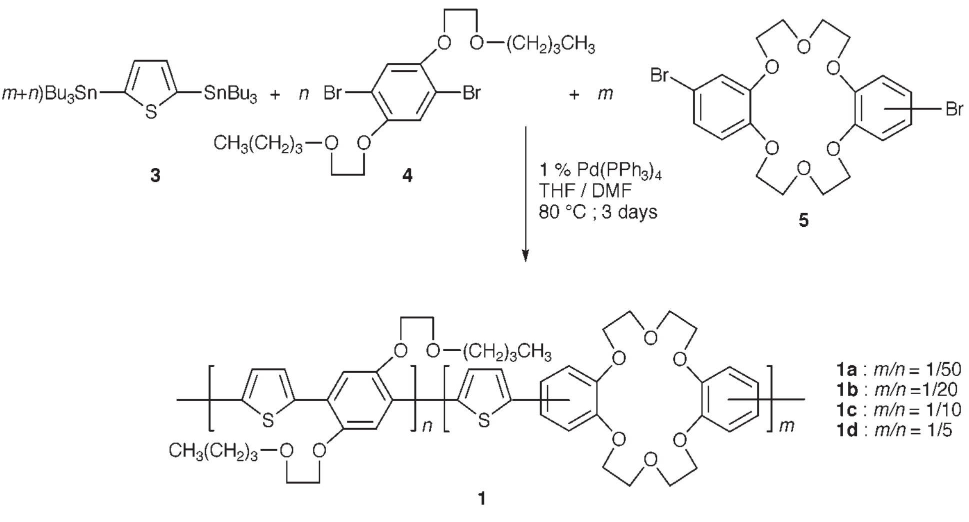
Here, we report the synthesis and the ionochromic behavior of [thienylene-*p*-(2,5-dialkoxy)-phenylene] copolymers which contain chelating units in the polymer backbone. We earlier showed that [thienylene-*p*-(2,5-dialkoxy)-phenylene] copolymers have interesting luminescent and electrochromic properties.[7] Moreover, owing to the presence of alkoxy substituents thin films on glass can be easily realized. In order to study their potential applications as ion sensors, we introduced in the polymer skeleton two types of chelating units: a crown ether for the complexation of alkali or alkaline earth metal ions and a 2,2′-bipyridine unit which easily forms complexes with transition metal ions.

Results and discussion

1. Polymers synthesis

The synthesis of the two polymers was based on the Stille coupling reaction between a dihalogeno aromatic substrate and a bis(tributylstannyl) aromatic species in the presence of Pd(0) as the catalyst. It has already proved to be an efficient route to regioregular poly(3-alkylthiophene).[8] Moreover, alternating thienylene-phenylene copolymers[9] have also been reported using a polycondensation based on the Stille coupling reaction.

Polymers **1** were synthesized by a co-condensation reaction using 2,5-bis(tributylstannyl)thiophene (**3**) with a known ratio of 1,4-dibromo-2,5-di(2-butoxyethoxy)benzene (**4**) and of 4,4′(5′)-dibromodibenzo-18-crown-6 ether (**5**). It gave soluble conjugated polymers in THF or $CHCl_3$ with alternating conjugated unit and coordinating entities (Scheme 1).



Scheme 1 Synthesis of copolymers **1**.

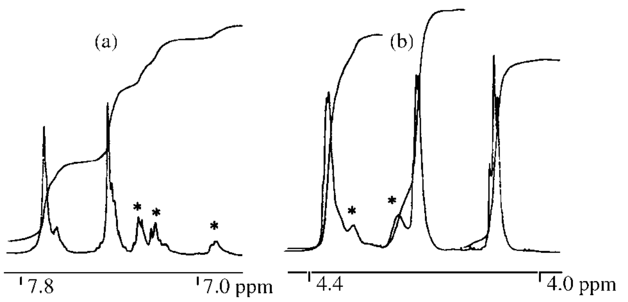


Fig. 1 ^{1}H NMR spectrum of coplymer **1d**. The asterisks indicate characteristic signals of the protons of the crown ether: a) aromatic protons region; b) aliphatic protons region.

The structure of polymers **1** was studied by ^{1}H NMR in $CDCl_3$. The relative intensities of the signals around $\delta = 7.2$–7.4 ppm and $\delta = 4$–4.4 ppm allow estimation of the average crown-ether content in the polymer chain. The values are very close to the ratio of the two dibromo monomers **4** and **5** used in the polycondensation with the tributyltin reagent (Scheme 1). The ^{1}H NMR spectrum of **1d** is given as an example (Fig. 1). This indicates that the two dibromo compounds **4** and **5** exhibit a similar reactivity towards the tin reagent **3** and their incorporation in the polymer chain follows the initial concentration ratio of the two monomers.

The molecular weights of polymers **1** were determined by size exclusion chromatography (SEC) (THF as eluent) with an on-line refractive index detector using polystyrene standards calibration. The measured average molecular weights M_w varied from 8.8×10^3 to 14×10^3 (Table 1). It suggested an average degree of polymerization (Dpn) varying from 12 to 26.

The UV–Vis spectra were recorded from 10^{-4} M solutions in $CHCl_3$ and from thin films on glass (Table 1).

The synthesis of polymer **2** is shown in Scheme 2.

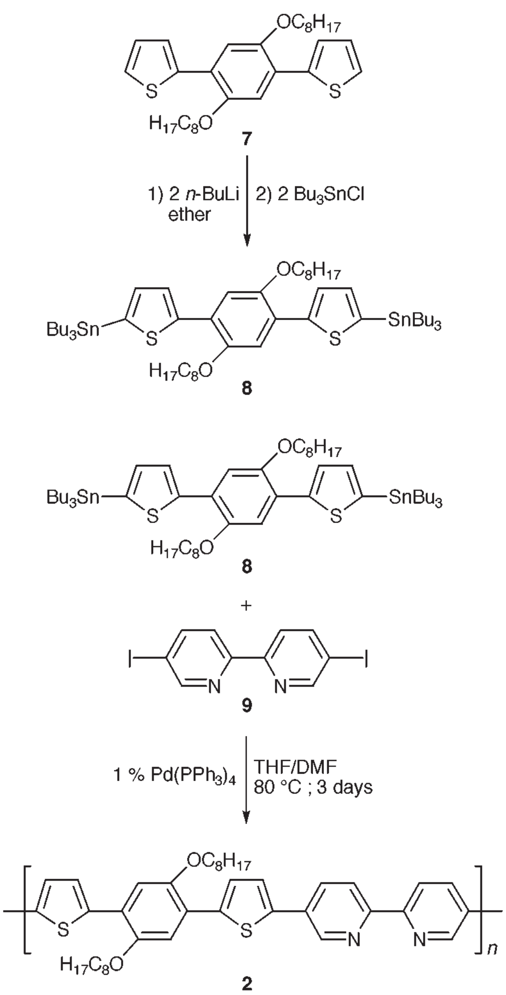
The monomer **7** was synthesized in 63% yield by palladium(0) ($Pd(PPh_3)_4$) catalysed coupling of 1,4-dibromo-2,5-di(octyloxy)benzene (**6**) with 2-thienylzinc chloride.[10] At 0 °C **7** was then metalated, in diethyl ether, using two equivalents of *n*-butyllithium and treated with two mole-equivalents of tributylstannyl chloride to give **8** in 60% yield. Finally, polymer **2** results from the palladium catalysed condensation between 5,5′-diiodo-2,2′-bipyridine[11] **9** and the bis(tributylstannyl) derivative **8**. The structure of polymer **2** was studied in $CDCl_3$ solution by ^{1}H NMR.

The molecular weight of polymer **2** was as previously measured by SEC experiment in THF eluent and the value refers to polystyrene standards: $M_w = 3477$, $M_w/M_n = 1.12$, Dpn = 5.

In the UV–Vis spectrum, the absorptions λ_{max} of polymer **2** are 438 nm ($\varepsilon_{\lambda_{max}} = 23250$) in a 10^{-5} M solution in $CHCl_3$ and 517 nm in a thin film on glass.

2. Ion responsive properties

2.1 Polymer 1. It has been recently shown that poly(alkylthiophene)s containing side chains functionalized with oligo(oxyethylene) or crown ether have ionoresponsive properties.[4,5b,12b,13,14] These ionoresponsive properties (*e.g.* ionochromism in the presence of alkali metals) are due to modification of the conformation of the coordinating side chain upon interaction with the metal ion. It induces a cooperative twisting of the main chain of the polymer and results in modifications of the conjugation and optical properties of the polymer. Cyclic voltammetry experiments performed with such conjugated polymers having side chains containing coordinating units showed variation in the oxidation potential when alkali metal ions were added. Moreover these materials exhibited ionochromic properties.[4,5b,12] We therefore examined the properties of polymers **1**.



Scheme 2 Synthesis of copolymer **2**.

A sample of polymer **1** was deposited on a platinum electrode by evaporation of a saturated THF solution. Cyclic voltammetry was then performed in MeCN (0.1 M Bu_4NPF_6; 50 mV s^{-1}). The observed variations of the oxidation potential: +35 and +60 mV, when Li^+ or K^+ were respectively added to polymer **1d**, were consistent with a weak coordination of these ions to the crown ether unit (Fig. 2).

However, we did not observe any ionochromic effect when Li^+ or K^+ ions were added to polymer **1** in a THF solution.

Table 1 Selected data for polymers **1**

Polymers of type **1**	M_w[a]	M_w/M_n	Dpn[b]	λ_{max}/nm (ε_{max})[c] $CHCl_3$ (10^{-4} M)	λ_{max}/nm Films on glass
1a	14093	1.35	26	459 (26010)	496
1b	10515	1.10	19	458 (24560)	490
1c	8878	1.25	16	455 (24304)	490
1d	8795	1.45	12	452 (23346)	488

[a] Determined by SEC using polystyrene standards. [b] Degree of polymerisation. [c] Measured in 10^{-4} M $CHCl_3$ solutions.

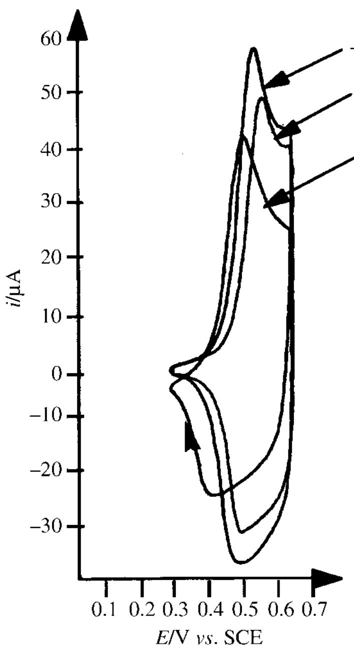


Fig. 2 Cyclic voltammetry of copolymer **1d**. Shift of the oxidation potential upon addition of Li^+ or K^+.

The absence of the ionochromic effect could be attributed to the structure of polymer **1**. The coordinating unit is not the side chain, but in the conjugated main chain. Complexation of metal ions by the dibenzo-18-crown-6 unit probably occurred, but it seems in this case that the interaction with the metal ion did not modify the length of the conjugated segment. It is possible that in this polymer, the change of the conformation of the dibenzo-18-crown-6 ether affected only weakly the conformation of the conjugated chain.

2.2 Polymer 2. We therefore explored the ion responsive properties of polymer **2** in which complexation of the bipyridine unit was expected to strongly modify the conjugation properties of the material.

Protonation–deprotonation. The protonation ability of polymer **2** was first observed in (10^{-5} M) $CHCl_3$ solutions. Addition of increasing amounts of a (1 M) $CHCl_3$ solution of trifluoroacetic acid (TFA) resulted in changes of the color of the solution. The solution, originally yellow ($\lambda_{max} = 425$ nm), became progressively pink ($\lambda_{max} = 492$ nm) (Fig. 3). After addition of 400 μL of TFA (1 M) no further changes were observed, the protonation of polymer **2** being completed.

Thin films of polymer **2** on a glass substrate were realized by slow evaporation of a saturated solution in $CHCl_3$. The UV–vis spectra showed an absorption maximum at $\lambda_{max} = 438$ nm. The same value was observed using a poly(ethylene) support. As previously observed with conjugated polymer,[15] in comparison to the solution behavior a red-shift of the absorption occurred when the polymer was analysed in the solid state. Exposure of the film of polymer **2** to HCl or HCOOH vapors induced a color change from brown to purple. It was characterized by a bathochromic displacement of the absorption maxima of $\Delta\lambda_{max} = 86$ nm (HCl vapor) and 33 nm (concentrated HCOOH). The shifts of the absorption maximum depended on the strength of the acid. When this purple film was then exposed to ammonia vapors, it turned brown again. These color changes characterize the reversible protonation–deprotonation process of the 2,2′-bipyridyl units in the main chain of polymer **2**. This phenomenon is associated with differences in the conformation of the 2,2′-bipyridyl unit in its protonated and unprotonated form.[3] The protonation of the 2,2′-bipyridyl units induces rotation of the two pyridyl rings, the planar conformation of the protonated bipyridine unit leads to an increase in the conjugation length of the polymer. In the unprotonated form the 2,2′-bipyridyl units have more twisted conformations and the mean conjugation length is lower.

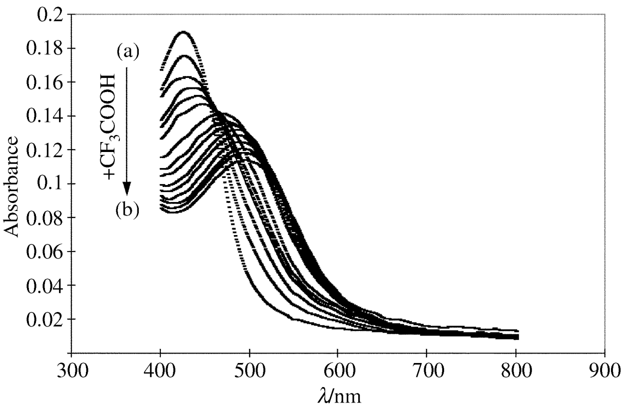


Fig. 3 Modification of the absorption spectrum of a 2 mL solution of copolymer **2** (10^{-5} M) upon addition of increasing amounts of a F_3CCOOH solution (1 M) (each spectrum corresponds to the successive addition of 20 μL of the acid solution): a) copolymer **2** alone; b) after addition to copolymer **2** of 400 μL of a F_3CCOOH solution (1 M).

The protonation–deprotonation cycle can be repeated at room temperature without any noticeable degradation of the film and without changes of its optical properties for at least five cycles. Interestingly, the color of polymer **2** can change continuously from yellow to pink in solution or from brown to purple for thin films in glass depending on the degree of protonation without measurable degradation of films during more than five cycles.

Transition metal ion responsive properties of polymer 2. The ionochromic effect of polymer **2** was characterized by instant color changes of the initially yellow solutions of polymer (10^{-5} M in $CHCl_3$) upon the addition of solutions of metal salts (10^{-4} M in $CHCl_3$). Fig. 4 shows the changes of color from yellow ($\lambda_{max} = 441$ nm) to pink–purple according to the nature of the ion. The absorption maxima varied from $\lambda_{max} = 473$ nm for Ag^+ ($AgBF_4$), $\lambda_{max} = 516$ nm for Cu^+ ($Cu(CH_3CN)_4PF_6$), $\lambda_{max} = 518$ nm for Zn^{2+} ($ZnCl_2$) and $\lambda_{max} = 543$ nm for Pd^{2+} ($PdCl_2$).

The ionochromic properties were also studied in the case of thin films. Thin orange films of polymer **2** were laid on a glass substrate upon slightly heating a few drops of a saturated

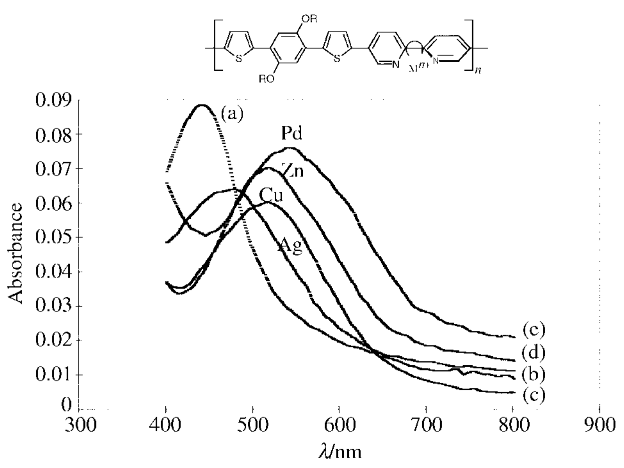


Fig. 4 Ionochromism of a solution of copolymer **2** in the presence of transition metal ions: a) copolymer **2**; b) with added Ag^+; c) with added Cu^+; d) with added Zn^{2+}; e) with added Pd^{2+}.

purple solution of polymer **2** in HCOOH. The IR spectrum of a film deposited under these conditions showed a weak absorption band attributed to formate at ν(C=O) = 1598 cm^{-1}. It is indicative of a partial protonation of polymer **2**. It showed an absorption maximum at $\lambda_{max} = 447$ nm. The samples were then dipped into 10^{-4} M solutions of various metal salts in $CHCl_3$. In all cases, whatever the metal ion (Pd^{2+}, Ag^+, Cd^{2+}, Zn^{2+}, Cu^+), a slight red-shift of the absorption maximum was recorded ($\lambda_{max} = 460$ nm). In the solid state, it showed a weak and unselective coordination of the 2,2′-bipyridyl subunits towards the metallic ions in polymer **2**. It may be related to a low accessibility of the bipyridine coordination site to the metal ion or to the partial protonation of the 2,2′-bipyridine units. We therefore studied a solvent of higher polarity than $CHCl_3$ in which metal ion salts are more soluble.

A similar experiment was performed using more concentrated transition metal ion solutions (1 M) in MeOH. In the absence of any metal ion a solvatochromism was observed since in MeOH the absorption maximum of polymer **2** shifts to $\lambda_{max} = 478$ nm. When orange films of polymer **2** were successively immersed in (1 M) solutions of metal salts in MeOH, the polymer color became blue. The observed absorption maxima were $\lambda_{max} = 490$ nm for Ag^+, 505 nm for Pd^{2+}, 520 nm for Zn^{2+} and Cd^{2+} and 530 nm for Cu^+. In this case, the ionochromism of polymer **2** appears even in the solid state. The bathochromic shift of the absorption maximum is indicative of an increase in the mean conjugation length of the polymer.

A lower value of $\Delta\lambda_{max}$ was however observed in the solid state ($\Delta\lambda_{max} = 50$ nm) compared to the previous value in solution ($\Delta\lambda_{max} = 80$ nm). This increase in the mean conjugation length is due to the planar conformation of the bidentate coordinating bipyridyl subunits in the polymer in the presence of transition metal ions.[2] Even if the red-shift in the absorption spectra due to conjugation enhancement is lower in a solid thin film than in solution, the films of polymer **2** appeared quite responsive to transition metal ions.

Moreover, films or solutions of polymer **2** containing coordinated Zn, or Cu ions were also treated with a methanolic ammonia solution (1.3 M). The polymer color changed instantaneously, and turned back to its original color: orange in the solid state and yellow when the sample is in solution. Absorption wavelengths identical to the initial values of around 440 nm for solutions and 480 nm for films were observed. Ammonia acts as a competitive ligand for metal ions and removes the metal from the complexing site of the polymer. The reversibility of the chelation properties of polymer **2** is an important criterion for the use of this ionosensitive polymer as a chemosensory material.

Conclusion

We reported the preparation of two types of conjugated alternating polymers containing in the main chain: chelating subunits to introduce complexing properties and thienylene-*p*-(2,5-dialkoxy)phenylene units to bring luminescent and electrochromic properties. Additionally the presence of dialkoxyphenylenes provides the ability to realize films on glass. The coordinating properties of the copolymers were investigated. When the chelating unit is a dibenzo-18-crown-6 ether, a weak coordination of Li^+ or K^+ ions was found and no ionochromic properties were observed in the presence of alkali metals. When 2,2′-bipyridyl is the coordinating entity, the copolymer exhibits reversible ionochromic responses in the presence of transition metal ions both in solution and in the solid state. The ionochromic properties were also found upon protonation–deprotonation of the copolymer in solution and in the solid state. On the basis of observed enhanced ionochromic properties, copolymer **2** appears to be a good candidate for the elaboration of ion sensory materials.

Experimental

$CHCl_3$, THF, DMF and hexane (SDS) were dried by distillation over phosphorus pentoxide, sodium benzophenone ketyl and CaH_2 respectively. 4,4′(5′)-Dibromodibenzo-18-crown-6 ether (Acros), 2-butoxyethanol and tributyltin chloride (Aldrich) were used without further purification.

^{1}H NMR spectra were recorded in $CDCl_3$ at 200 MHz with a 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 spectrometer using $CDCl_3$ ($\delta = 77.70$ ppm) as the internal standard. ^{118}Sn NMR spectra were recorded in $CDCl_3$ at 93.27 MHz with a Bruker AC 250 spectrometer. IR spectra were recorded with a Perkin Elmer 1000 spectrometer. Melting points were measured with an Electrothermal 9100 apparatus. Absorption spectra were recorded on an MC^2 Safas spectrometer and emission spectra on an SLM-Aminco MC 200 spectrometer. SEC measurements were realized on a Waters device equipped with HR_2 and HR_3 Styragel columns. Cyclic voltammetry was realised on an EGG potentiostat connected to a Kipp & Zonen tracer.

Tetrakis(triphenylphosphine)palladium

This compound was prepared according to the literature.[16]

2,5-Bis(tributylstannyl)thiophene (3)

This compound was prepared according to the literature.[17]

1,4-Dibromo-2,5-dioctoxybenzene (6)

This compound was prepared according to the literature.[18]

5,5′-Diiodo-2,2′-bipyridine (9)

This compound was prepared according to the literature.[11]

1,4-Bis(2-butoxyethoxy)benzene (4a)

Under a nitrogen atmosphere, 2.07 g (0.090 mole) of sodium metal were gradually introduced into a Schlenk tube containing 50 mL of 2-butoxyethanol. When the sodium had completely reacted, 7.07 g (0.030 mole) of *p*-dibromobenzene, 2.5 g (0.032 mole) of copper(I) oxide and 0.1 g (0.003 mole) of potassium iodide were quickly added. The mixture was heated at 100 °C for 24 h then a new portion of potassium iodide (0.1 g; 0.003 mole) was introduced and the mixture was heated again at 100 °C for 24 h. The solution was filtered over Celite at room temperature, hydrolysed and extracted three times with diethyl ether. The organic layers were dried over magnesium sulfate, concentrated under vacuum and the residual oil was recrystallized in ethanol to give white crystals. Yield 20%, mp 28–29 °C. Found: C, 69.67; H, 9.76; O, 20.59%. $C_{18}H_{30}O_4$ requires C, 69.64; H, 9.74; O, 20.61%. δ_H ($CDCl_3$): 0.92 (6 H, t, 2 CH_3), 1.37 (4 H, m, 2 CH_2), 1.55 (4 H, m, 2 CH_2), 3.52 (4 H, t, 2 CH_2), 3.74 (4 H, t, 2 OCH_2), 4.06 (4 H, t, 2 OCH_2), 6.84 (4 H, s, 4 CH_{ar}). δ_C ($CDCl_3$): 13.93 (2 CH_3), 19.27, 31.72 (4 CH_2), 68.08, 69.29, 71.37 (6 OCH_2), 115.58 (4 CH), 153.15 (2 C).

1,4-Dibromo-2,5-bis(2-butoxyethoxy)benzene (4b)

1.88 g (0.0060 mole) of **4a** in solution in 10 mL of carbon tetrachloride were placed in a 100 mL magnetic stirred tricol equipped with a condenser and an isobar dropping funnel. Br_2 (0.62 mL, 0.0121 mole) was added dropwise from the funnel at room temperature. The mixture was stirred for 3 h at room temperature and then treated with 15 mL of a 20% solution of KOH in water. After three extractions with diethyl ether, the organic layers were dried over magnesium sulfate, concentrated *in vacuo* and the residual solid was recrystallized with ethanol to give colorless plates. Yield 61%, mp 42.5–43.8 °C. Found: C, 46.18; H, 6.04; O, 13.64%. $C_{18}H_{28}O_4Br_2$ requires C, 46.17; H, 6.02; O, 13.67%. δ_H ($CDCl_3$): 0.90 (6 H, t, 2 CH_3), 1.37 (4 H, m, 2 CH_2), 1.59 (4 H, m, 2 CH_2), 3.54 (4 H, t, 2 CH_2), 3.77 (4 H, t, 2 OCH_2), 4.10 (4 H, t, 2 OCH_2), 7.15 (2 H, s, 2 CH_{ar}). δ_C ($CDCl_3$): 13.93 (2 CH_3), 19.28, 31.79 (4 CH_2), 69.06, 70.23, 71.52 (6 OCH_2), 111.40 (2 C, C_1, C_4), 119.27 (2 CH, C_3, C_6), 150.38 (2 C, C_2, C_5).

1,4-Bis(2-thienyl)-2,5-dioctoxybenzene (7)

Under a nitrogen atmosphere, 7.14 mL (0.0178 mole) of a 2.5 M solution of *n*-butyllithium in hexane were slowly introduced at 0 °C, into a Schlenk tube containing thiophene (1.008 g; 0.012 mole) dissolved in 20 mL of freshly distilled THF. After stirring for 60 min at room temperature, the obtained 2-thienyllithium solution was slowly added to a $ZnCl_2$ (2.42 g; 0.0178 mole) suspension in 17 mL of THF and the mixture was magnetically stirred at room temperature for 1 h. This solution was then slowly added to a solution of **4b** (3 g, 0.0061 mole) and $Pd(PPh_3)_4$ (0.14 g, 0.000122 mole) in 20 mL of THF. When the addition was complete, the reaction mixture was refluxed for 72 h. After cooling, the medium was hydrolysed with a 1.5 M HCl solution. After three extractions with diethyl ether, the organic layers were twice washed with water and dried over $MgSO_4$ and concentrated *in vacuo* before recrystallisation from an ethanol–benzene mixture 3 : 1. Yield: 73%, mp 84-86 °C. δ_H ($CDCl_3$): 0.9 (6 H, t, 2 CH_3), 1.33 (20 H, m), 1.92 (4 H, t), 4.1 (4 H, t), 7.24 (2 H, s), 7.11 (2 H, m), 7.34 (2 H, d), 7.55 (2 H, d). δ_C ($CDCl_3$): 14.12, 22.68, 26.24, 29.34, 29.4, 29.5, 31.84, 69.77, 112.9, 123.1, 125.2, 125.6, 126.7, 139.3, 149.3.

2′,5′-Bis(tributylstannyl)[1,4-bis(2-thienyl)-2,5-dioctoxybenzene] (8)

Under a nitrogen atmosphere, 3.7 mL (0.006 mole) of a 1.6 M solution of *n*-butyllithium in hexane were introduced at 0 °C, into a Schlenk tube containing **7** (1.5 g; 0.003 mole) dissolved in 10 mL of freshly distilled diethyl ether. After stirring for two hours at room temperature, Bu_3SnCl (3.7 mL; 0.006 mole) in 10 mL of diethyl ether was slowly added at 0 °C to the mixture which was then stirred for one hour at room temperature. Ether was evaporated and the residue was treated with pentane. The solution was filtered and concentrated *in vacuo*; **3** was obtained as a yellow oil. Yield: 60%. δ_H ($CDCl_3$): 0.91 (24 H, t), 1.20 (12H, t), 1.26 (24 H, m), 1.34 (20 H, m), 1.9 (4 H, m), 4.06 (4 H, T), 7.16 (2H, d), 7.25 (2 H, s), 7.67 (2 H, d). δ_C ($CDCl_3$): 10.56, 13.70, 14.30, 22.5, 26.9, 29.1, 29.2, 29.3, 29.35, 31.7, 69.4, 112.6, 122.6, 126.1, 134.9, 137, 145, 148.9. δ_{Sn} ($CDCl_3$): −40.7.

Copolymers 1

All copolymers **1** were synthesized according to the same experimental procedure. The only changes that led to the four different polymers of type **1** concern the relative ratios between the two dibromo monomers engaged and the experimental description is detailed in the case of **1a** as an example.

Copolymer 1a

In a 50 mL Schlenk tube equipped with a condenser were dissolved under a nitrogen atmosphere and at room temperature 0.0115 g (10^{-5} mole) of $Pd(PPh_3)_4$ in 10 mL of a THF–DMF (50 : 50) solvent mixture. 0.001 mole (0.6622 g) of **3**, 98×10^{-5} mole (0.4588 g) of **4b** and 2×10^{-5} mole (0.0103 g) of **5** 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 adding acetone. The powder was filtered, washed with acetone and dried *in vacuo* to give 0.427 g of **1a** (Yield: 90%). Found: C, 66.4; H, 7.68; S, 8.24%. δ_H ($CDCl_3$): 0.92 (6 H, t, 2 CH_3), 1.43 (4 H, m, 2 CH_2), 1.63 (4 H, t, 2 CH_2), 3.58 (4 H, t, 2 OCH_2), 3.91 (4 H, t, 2 OCH_2), 4.30 (4 H, t, 2 OCH_2), 7.34 (2 H, s, 2 $CH_{thienyl}$), 7.63 (2 H, s, CH_{ar}). ν_{max}(KBr)/cm^{-1}: 3067, 2956, 2930, 2866, 1602, 1542, 1491, 1458, 1405, 1263, 1216, 1122, 1060, 850, 797. Absorption: λ_{max} ($CHCl_3$)/nm (ε_{max}/l mol^{-1} cm^{-1}) 459 (26 010), λ_{max} (film on glass) 496 nm. Emission: λ_{max} ($CHCl_3$) 521 nm, λ_{max} (film on glass) 567 nm.

Copolymer 1b

Copolymer **1b** was prepared from 0.001 mole (0.6622 g) of **3**, 95×10^{-5} mole (0.445 g) of **4b** and 5×10^{-5} mole (0.0259 g) of **5**. Yield: 90% (0.428 g). Found: C, 67.5; H, 7.62; S, 8.16%. δ_H ($CDCl_3$): 0.92 (6 H, t, 2 CH_3), 1.43 (4 H, m, 2 CH_2), 1.63 (4 H, t, 2 CH_2), 3.58 (4 H, t, 2 OCH_2), 3.91 (4 H, t, 2 OCH_2), 4.30 (4 H, t, 2 OCH_2), 7.34 (2 H, s, 2 $CH_{thienyl}$), 7.63 (2 H, s, CH_{ar}). ν_{max}(KBr)/cm^{-1}: 3068, 2956, 2930, 2865, 1600, 1540, 1492, 1451, 1406, 1262, 1215, 1122, 1060, 846, 797. Absorption: λ_{max} ($CHCl_3$)/nm (ε_{max}/l mol^{-1} cm^{-1}) 458 (24 560), λ_{max} (film on glass) 490 nm. Emission: λ_{max} ($CHCl_3$) 520 nm, λ_{max} (film on glass) 570 nm.

Copolymer 1c

Copolymer **1c** was prepared from 0.001 mole (0.6622 g) of **3**, 90.9×10^{-5} mole (0.426 g) of **4b** and 91×10^{-6} mole (0.0466 g) of **5**. Yield: 90% ($m = 0.430$ g). Found: C, 67.41; H, 7.54; S, 8.09%. δ_H ($CDCl_3$): 0.92 (6 H, t, 2 CH_3), 1.43 (4 H, m, 2 CH_2), 1.63 (4 H, t, 2 CH_2), 3.58 (4 H, t, 2 OCH_2), 3.91 (4 H, t, 2 OCH_2), 4.30 (4 H, t, 2 OCH_2), 7.34 (2 H, s, 2 $CH_{thienyl}$), 7.63 (2 H, s, CH_{ar}). ν_{max}(KBr)/cm^{-1}: 3070, 2955, 2930, 2866, 1600, 1540, 1492, 1451, 1406, 1263, 1218, 1119, 1060, 847, 796. Absorption: λ_{max} ($CHCl_3$)/nm (ε_{max}/l mol^{-1} cm^{-1}) 455 (24 304), λ_{max} (film on glass) 490 nm. Emission: λ_{max} ($CHCl_3$) 520 nm, λ_{max} (film on glass) 566 nm.

Copolymer 1d

Copolymer **1d** was prepared from 0.001 mole (0.6622 g) of **3**, 83.3×10^{-5} mole (0.3900 g) of **4b** and 16.7×10^{-5} mole (0.0855 g) of **5**. Yield: 90% ($m = 0.433$ g). Found: C, 67.26; H, 7.33; S, 8.01%. δ_H ($CDCl_3$): 0.92 (6 H, t, 2 CH_3), 1.43 (4 H, m, 2 CH_2), 1.63 (4 H, t, 2 CH_2), 3.58 (4 H, t, 2 OCH_2), 3.91 (16/5 H, t, 8/5 OCH_2), 3.99 (8/5 H, t, 4/5 OCH_2), 4.19 (8/5 H, t, 4/5 OCH_2), 4.30 (16/5 H, t, 8/5 OCH_2), 6.63 (2/5H, s, $H_{crown\text{-}ether}$), 7.13 (2/5H, d, $H_{crown\text{-}ether}$), 7.20 (2/5H, d, $H_{crown\text{-}ether}$), 7.34 (8/5 H, s, $CH_{thienyl}$), 7.57 (2/5H, s, $H_{thienyl}$), 7.63 (2 H, s, CH_{ar}). ν_{max}(KBr)/cm^{-1}: 3067, 2955, 2926, 2861, 1600, 1538, 1494, 1453, 1451, 1403, 1263, 1216, 1122, 1042, 844, 795. Absorption: λ_{max} ($CHCl_3$)/nm (ε_{max}/l mol^{-1} cm^{-1}) 452 (24 304), λ_{max} (film on glass) 488 nm. Emission: λ_{max} ($CHCl_3$) 520 nm, λ_{max} (film on glass) 561 nm.

Polymer 2

In a 100 mL Schlenk tube equipped with a condenser were dissolved under a nitrogen atmosphere and at room temperature 0.022 g (2.10^{-5} mole) of $Pd(PPh_3)_4$ in 20 mL of a THF–DMF (50 : 50) solvent mixture. 0.002 mole (2.152 g) of **3** and 0.002 mole (0.816 g) of **9** 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 adding methanol. The powder was filtered, washed with acetone and dried *in vacuo*. δ_H ($CDCl_3$): 0.07 (6 H, t, 2 CH_3), 0.88 (4 H, m, 2 CH_2), 1.32 (4 H, m, 2 CH_2), 1.58 (4 H, m, 2 CH_2), 4.17 (4 H, m, 2 OCH_2), 7.29 (2 H, s, 2 $CH_{thienyl}$), 7.44 (2 H, s, CH_{ar}), 8.5 (2 H, dd, H_{pyr}), 9 (1 H, d, H_{pyr}). ν_{max}(KBr)/cm^{-1}: 2915, 2848, 1601, 1572, 1535, 1502, 1454, 1406, 1262, 1211, 1089, 835, 794. Absorption: λ_{max} ($CHCl_3$)/nm (ε_{max}/ l mol^{-1} cm^{-1}) 438, λ_{max} (film on glass) 517 nm.

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