Regiochemistry and Conformation of Poly(3-hexylthiophene) *via* the Synthesis and the Spectroscopic Characterization of the Model Configurational Triads

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ABSTRACT: The four model configurational triads of poly(3-hexylthiophene) (PHT) were synthesized by cross-coupling of the appropriate stannyl and bromo 3-hexylthiophene derivatives, catalyzed by $Pd[(C_6H_5)_3P]_4$. The comparison of ^1H and ^{13}C NMR chemical shifts of the triads with those of PHT allows the unambiguous assignment of the regiochemistry of the polymer. The NMR data of the triads, in conjunction with the results of force field MMP2 calculations, also give information on the conformational properties of PHT samples of different regiochemistry.

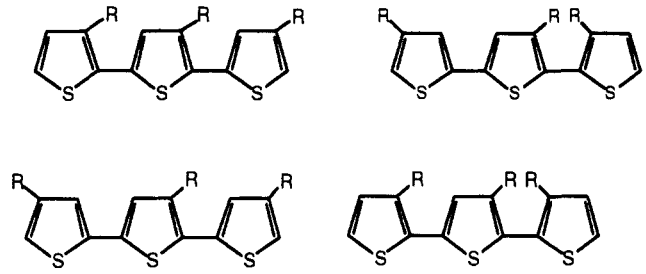
α-Conjugated oligo- and polythiophenes are currently receiving considerable attention in research on conducting polymers and molecular electronics. The interest is especially directed toward the introduction of side chains for solubility improvement and the building up of regioregular structures for the modulation of the electrical and optical properties of these materials.[1]

There is experimental evidence that the substitution pattern, *i.e.*, the regiochemistry, of substituted polythiophenes controls their conformational features, which, in turn, govern the degree of $\pi-\pi$ conjugation between adjacent rings, and hence the electrical and optical properties of the polymers.[1] An unambiguous way of establishing the regiochemistry of a substituted polythiophene is through the synthesis of the corresponding configurational triads[2] and the comparison of their spectroscopic features (^1H and ^{13}C NMR, in particular) with those of the polymer. The model triads, which are four different regioisomers of trisubstituted 2,2′:5′,2″-terthiophene (*cf.* Chart 1), represent all the possible modes in which a central 3-substituted thiophene unit can be α,α'-coupled to two similar units *via* the 2- and 5-positions, either head-to-tail (HT), tail-to-tail (TT), or head-to-head (HH).

So far, no attempts have been made to synthesize the configurational triads of substituted polythiophenes. In principle, a variety of conditions could be employed for the synthesis of the triads, starting from 3-substituted thiophene and generating new carbon–carbon bonds by nickel- or palladium-catalyzed cross-coupling of thienyl bromides with thienyl organometallics such as zinc, boronic acid, and tin reagents.[3] Although organotin reagents are extensively employed due to their synthetic potential,[4] they have been scarcely used in the synthesis of substituted oligothiophenes. The more generally employed reaction for the preparation of oligothiophenes is the cross-coupling of thienyl bromides with thienylmagnesium bromides in the presence of nickel catalysts.[5] This reaction, however, gives very low yields when the thienyl derivatives to be cross-coupled bear long alkyl chains next to the reaction site.

Reported herein is the synthesis, based on the use of tin derivatives, of the model triads (compounds 1–4) of poly-(3-hexylthiophene) (PHT), which is one of the most investigated polythiophenes because of its peculiar solvatochromic and thermochromic properties.[6] A few papers have been recently published describing new synthetic routes for the preparation of various versions of this polymer having different physicochemical properties.[7–10]

Chart 1. Configurational Triads of Poly(3-R-thiophene)



In this paper the ^{13}C and ^1H NMR chemical shifts of triads 1–4 are used to establish the regiochemistry of a sample of poly(3-hexylthiophene) prepared by oxidative polymerization of 3-hexylthiophene with ferric chloride and to discuss the substitution pattern of a regiorandom version of PHT whose ^{13}C and ^1H NMR chemical shifts have recently been reported.[7] Also given in this paper are a few indications, based on NMR data and supported by MMP2 calculations, about the conformational properties of 1–4 and of the corresponding configurational segments in poly(3-hexylthiophene).

Results and Discussion

(I) Synthesis and Spectroscopic Characterization of the Configurational Triads of Poly(3-hexylthiophene). The synthetic method used for the synthesis of triads 1–4 is outlined in Scheme 1 and is based on selective mono- and dibromination of 3-hexylthiophene with *N*-bromosuccinimide in chloroform, selective metalation of 3-hexylthiophene with BuLi/TMEDA followed by quenching with trimethyltin chloride and cross-coupling of the tin derivative with the appropriate thienyl bromide in the presence of tetrakis(triphenylphosphine)palladium. The cross-coupling reaction affords nonnegligible amounts of product formed by homocoupling of the tin derivative. Purification of the reaction mixture, which may also involve

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Scheme 1. Synthesis of Triads 1–4 [R = $(CH_2)_5CH_3$]

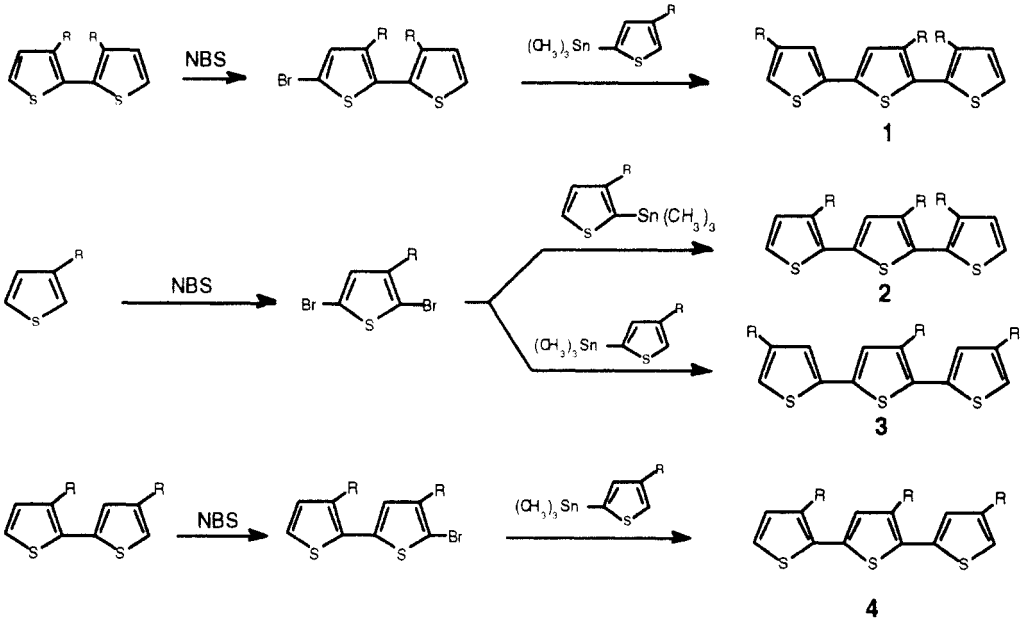


Table 1. ^1H Chemical Shifts[a] of the Aromatic Region of the Model Triads of PHT (1–4)

TT-HH (1)	H5	H3	**H3′**	H4″	H5″
	6.77	6.99	**7.00**	6.95	7.27
HT-HH (2)	H5	H4	**H3′**	H4″	H5″
	7.15	6.93	**6.98**	6.95	7.30
TT-HT (3)	H5	H3	**H3′**	H3″	H5″
	6.76	7.00	**6.96**	6.94	6.86
HT-HT (4)	H5	H4	**H3′**	H3″	H5″
	7.12	6.90	**6.92**	6.96	6.87

[a] In ppm, in $CDCl_3$.

separation of different regioisomers, could only be achieved by flash chromatography using reverse phase RP 18 silica gel. The ^1H and ^{13}C chemical shifts, in deuteriated chloroform, of the aromatic region of 1–4 are given in Tables 1 and 2, respectively. Figure 1 shows the aromatic region of the 2D HETCOR spectra of the model triads and illustrates the connectivity pattern existing between the ^1H and the ^{13}C spectra of these regioisomers.

The assignment of H3′, the proton belonging to the central unit of compounds 1–4, is straightforward, since it gives rise to the only singlet present in the spectrum. Table 1 shows that its chemical shift varies within a very small range (6.92–7.00 ppm) when the type of α,α' linkage with the adjacent thiophene units changes from HT to TT or HH. The assignment of the remaining aromatic protons of 1–4 is made on the basis of the well-known features of thiophene derivatives, according to which protons separated by three bonds, such as H4,H5 or H4″, H5″, are characterized by $^3J_{AB}$ coupling constants on the order of 5 Hz, while protons separated by four bonds, such as H3,H5 or H3″,H5″, are characterized by $^4J_{AB}$ coupling constants on the order of 2–3 Hz. The assignment of the carbon resonances of 1–4 is not as easy as that of proton resonances. A first assignment was made on the basis of the chemical shifts of the three diads of PHT, namely, 3,3′-, 3,4′-, and 4,4′-di(3-hexyl)-2,2′-bithiophene,[11] and then checked with the aid of 2D HETCOR experiments (*cf.* Figure 1). Furthermore, the assignment was confirmed by HMQC and HMBC inverse-detection ^{13}C NMR experiments.[12] As already observed,[13] the ^{13}C chemical shifts of oligothiophenes are insensitive to the conjugation degree of these systems but are very dependent on the position of the alkyl substituents. Thus, ^{13}C NMR is an extremely useful technique to establish the regiochemistry and the conformation of oligothiophenes.

Table 2 shows that the change of the type of α,α' linkage leads to variations of the chemical shifts of *all* of the four carbons of the central unit of 1–4, which are much greater than those observed in proton spectra. Moreover, it is seen that a configurational change—in one or the other of the two linkages—of the type TT → HT (such as that needed to pass from 1 to 2 or from 3 to 4) or HH → HT (such as that needed to pass from 1 to 3 or from 2 to 4), leads to $\delta(^{13}C)$ increments which are almost independent of the nature of the adjacent junction. This is summarized in Scheme 2, which gives the sign and the magnitude of $\delta(^{13}C)$ increments for the HT → TT, HH → HT, TT → HT, and HT → HH configurational changes occurring in one or the other of the two junctions. It should be noticed that this scheme allows the prediction of the ^{13}C NMR spectrum of the aromatic region of PHT in all its regiochemically different forms.

(II) Assignment of the Regiochemistry of PHT by ^1H and ^{13}C NMR. Figure 2 reports the proton spectrum (in chloroform) of the aromatic region of a sample of PHT obtained by oxidative polymerization of 3-hexylthiophene with ferric chloride, prepared according to the modalities described in ref 10. The aromatic region of the spectrum consists of a major peak at 6.98 ppm, which accounts for about 80% of the total signal intensity, and of three minor peaks of nearly equal intensities at 7.05, 7.03, and 7.00 ppm. This spectrum has the same chemical shifts and the same relative peak intensities as those reported by Sato *et al.* for a sample of electrochemically prepared poly(3-dodecylthiophene) (PDDT).[2] It has also the same chemical shifts (but not the same relative intensities) as the spectrum of a regiorandom sample of PHT[7] and of different samples of PHT obtained with diverse synthetic methods.[10,14] Comparison of the proton chemical shifts of our PHT sample with the values of the chemical shifts of the H3′ proton of the four configurational triads, reported in Table 1, shows that all the protons of the polymer sample are *deshielded* by about 0.05 ppm with respect to the H3′ protons of triads 1–4. The constancy of the deshielding effect suggests that the assignment of the peaks of the PHT sample to the four configurations should follow the same order as that observed for compounds 1–4 *i.e.*, that the major peak at 6.98 ppm should be attributed to the

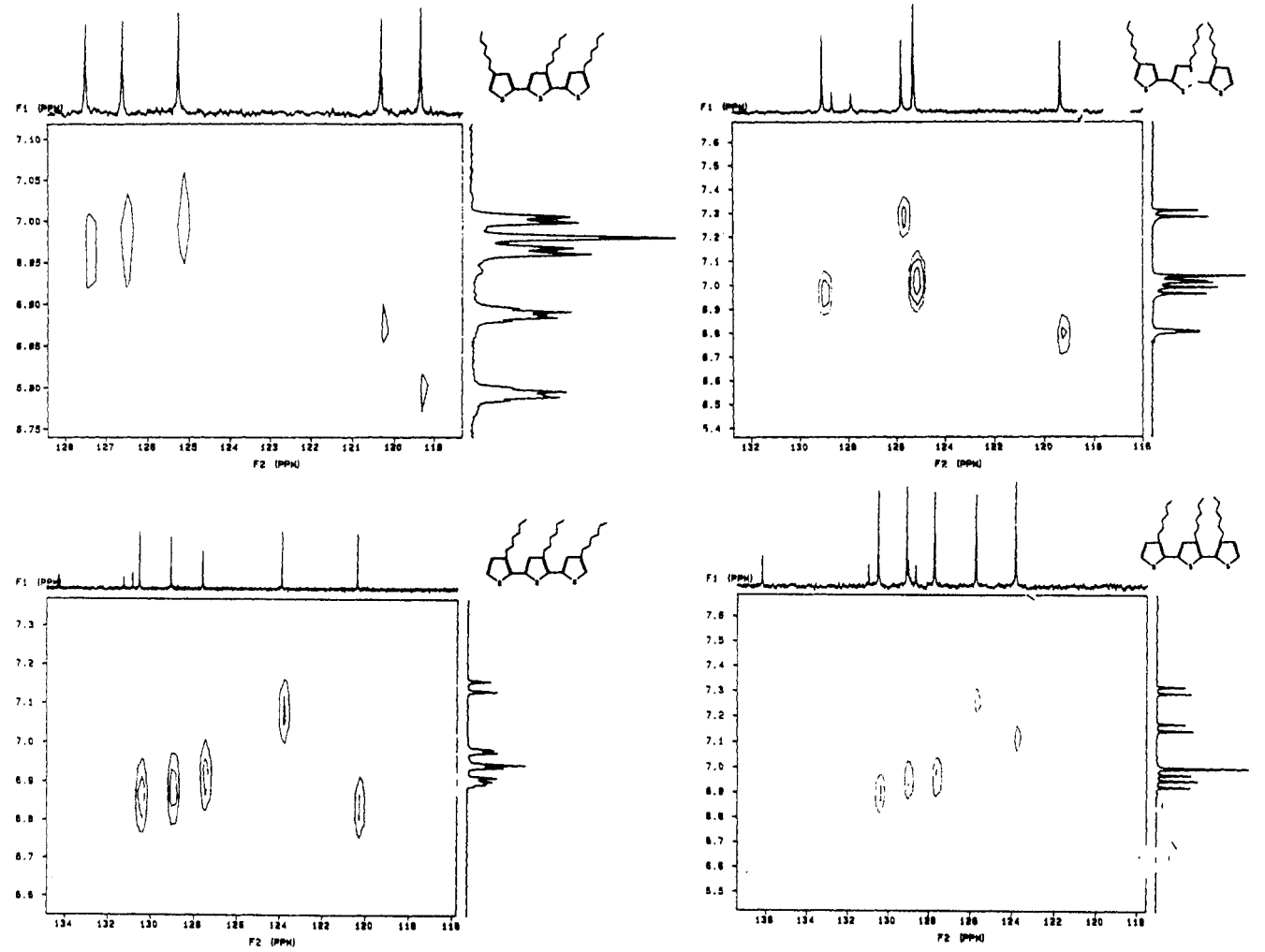


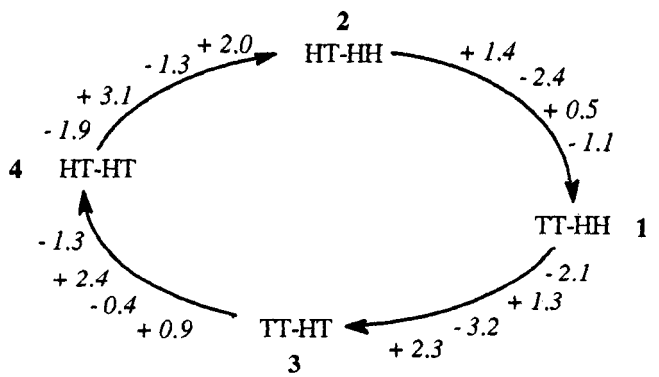
Figure 1. Two-dimensional HETCOR spectra of the aromatic region of model triads 1–4, illustrating the proton–carbon connectivities of the four regioisomers.

Table 2. ^{13}C Chemical Shifts[a] of the Aromatic Region of the Model Triads (1–4) of PHT

	C2	C3	C4	C5	C2′	C3′	C4′	C5′	C2″	C3″	C4″	C5″
TT–HH (1)	137.1	124.9	144.1	118.9	**137.3**	**124.9**	**143.1**	**127.5**	128.4	142.5	128.6	125.4
HT–HH (2)	130.9	139.4	130.0	123.4	**135.9**	**127.3**	**142.6**	**128.6**	128.5	142.5	128.6	125.5
TT–HT (3)	136.9	124.8	144.1	118.9	**135.2**	**126.2**	**139.9**	**129.8**	135.7	127.1	143.6	119.9
HT–HT (4)	131.0	139.5	130.0	123.5	**133.9**	**128.6**	**139.5**	**130.7**	135.6	127.1	143.6	120.0

[a] In ppm, in $CDCl_3$.

Scheme 2. ^{13}C Chemical Shift Increments (in ppm) of the Central Unit of Triads 1–4, Following a Configurational Change H → T or T → H in One of the Two Adjacent Junctions.[a]



[a] The increments are those relative to C2′, C3′, C4′, and C5′ (from top to bottom).

HT–HT configuration, the one at 7.00 ppm to the TT–HT configuration, the one at 7.03 ppm to the HT–HH configuration, and the one at 7.05 ppm to the TT–HH configuration. This assignment is in agreement with that made by Holdcroft *et al.*[8] on the basis of qualitative arguments on conformation-dependent ring current effects on the $\delta(^1H)$ values of the aromatic region of PHT. However, they are in contrast with other authors[9,14] as far as the assignment of TT–HT and HT–HH configurations is concerned. Thus, up to this point, a margin of ambiguity in the assignment of the different configurational portions of PHT by proton NMR still exists. However, the ambiguity can be removed by looking at the $\delta(^{13}C)$ values of PHT, which are insensitive to ring currents affecting proton chemical shifts. In the ^{13}C spectrum of the aromatic region of our PHT sample, which is the same as that reported by other authors,[10,14] only the four signals pertaining to the major component of the polymer (139.9, 133.8, 130.5, and 128.7 ppm) are clearly assignable whereas some of the signals pertaining to the minor components are not sufficiently intense. However, the ^{13}C spectrum of the aromatic region of PHT in its four different configurations has been recently reported by Riecke *et al.*,[7] who have been able to prepare a totally regiospecific

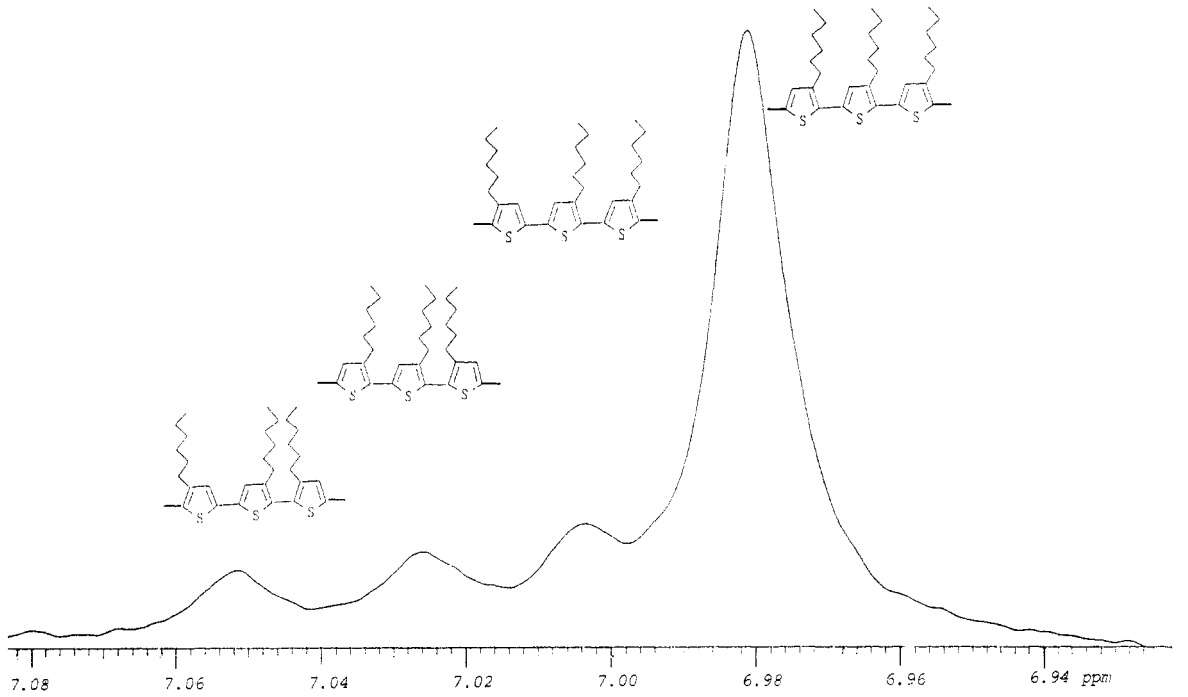


Figure 2. ^{1}H NMR spectrum of the aromatic region of a sample of poly(3-hexylthiophene) obtained by action of $FeCl_3$ on 3-hexylthiophene.

HT–HT version of PHT as well as a regiorandom 1:1:1:1 HT–HH:TT–HT:TT–HH:HT–HT version of the same polymer having different electrical and optical properties. The $\delta(^{13}C)$ values given by Riecke *et al.* match closely those of the central units of triad **1–4**, although the assignment made by the authors for carbons C2′ to C5′ within a given triad is incorrect. Comparison of Riecke's data with the chemical shifts of the central units of compounds **1–4** shows that the assignment made for the TT–HT and HT–HH configurations should be interconverted. Riecke *et al.* with the aid of their regiorandom samples were also able to associate each $\delta(^{13}C)$ set to its own proton (H3′) resonance. Interconversion of the proton resonance of the HT–HH and TT–HT configurations leads to the assignment made by us and by Holdcroft for the four configurational varieties of PHT. A look at the proton chemical shifts of the external units of compounds **1–4** (*cf.* Table 1) shows that the assignments made by Holdcroft of the proton chemical shifts of the four possible terminal units of PHT is correct, too. The present results suggest that even the assignment of HT–HH and TT–HT configurations of PDDT should be interconverted.[2] In fact, the proton chemical shifts of the aromatic region of PDDT are the same as those of PHT and, in consequence, the effects of substituent chain length on conformation cannot be invoked. The misunderstanding could arise from a mistake in the assignment of the chemical shift of the α-methylene protons of the aliphatic chains in the different configurations.[15]

(III) Conformational Analysis of the Configurational Triads and of the Corresponding Configurational Segments of PHT. The ^{13}C chemical shifts given in Table 2 for the central unit of the model triads **1–4** and those given in ref 7 for PHT are remarkably similar. Since ^{13}C chemical shifts are very sensitive to conformational variations,[13] this indicates that, in chloroform, the conformation of the different configurational segments of PHT must be similar to that of triads **1–4**. Moreover, the fact that in triads **1–4** the $\delta(^{13}C)$ increments for a given configurational change are independent of the nature (HT or TT or HH) of the side junction not involved in the change can be taken as an indication that the conformation of this very junction is also independent of the nature of the other one. Thus, we have undertaken a MMP2 study of the conformation of compounds **1–4**, using a value of the dielectric constant of the medium, $\epsilon = 5$, close to the dielectric constant of chloroform. The results are reported in Table 3, which, for comparison, also gives the calculated conformational energies and populations of **1–4** for $\epsilon = 1.5$. In agreement with ^{13}C NMR data, Table 3 shows that, on going from **1** to **2** or from **3** to **4**, the configurational variation TT → HT leads the junction involved in this change from a prevalently *cis* planar conformation to a prevalently *trans* tilted conformation in both cases. Likewise, on going from **1** to **3** or from **2** to **4**, the configurational variation HH → HT leads the junction involved in the change from a prevalently *trans* tilted conformation to another prevalently *trans* tilted conformation. Thus, from the point of view of the conformational

Table 3. MMP2[a] Calculated Conformational Energies (*E*, kcal mol^{-1}), Inter-ring Twist Angles (ω, deg),[b] Populations (*p*, %), and Experimental[c] and Calculated[d] (PPP) λ_{max} Values of the Model Triads 1–4

	ω_1	ω_2	$E_{1,5}$	$p_{1,5}$	E_5	p_5	$\lambda_{max}{}^c$	$\lambda_{max}{}^d$
TT–HH 1							326	
syn–anti	0	±134	46.18	30	44.64	85		325
anti–anti	±149	±134	46.07	35	46.14	7		
anti–anti	∓148	±134	46.07	35	46.05	8		
HT–HH 2							315	
syn–anti	0	±133	49.72	0	48.01	2		
anti–anti	±140	±135	47.73	3	47.93	2		
anti–anti	∓133	±129	45.63	97	45.67	96		300
TT–HT 3							348	
syn–syn	0	0	47.10	0	43.27	16		363
anti–syn	±149	0	46.41	1	44.56	4		
syn–anti	0	±140	44.41	30	42.83	68		337
anti–anti	±147	±139	44.31	36	44.31	6		
anti–anti	±151	∓139	44.35	33	44.30	6		
HT–HT 4							336	
syn–syn	0	0	50.72	0	46.69	5		
syn–anti	0	±141	48.02	1.5	46.28	20		337
anti–syn	±141	0	48.02	1.5	46.28	20		337
anti–anti	±140	±138	45.92	55	46.04	30		312
anti–anti	±138	∓142	46.09	42	46.13	25		312

[a] Force field calculations using the N. L. Allinger program MM2(91) for two different values of the dielectric constant ($\epsilon = 1.5$, $\epsilon = 5$).[b] ω_1 = dihedral angle 322′3′; ω_2 = dihedral angle 4′5′2″3″. [c] In $CHCl_3$. [d] Parison–Parr–Pople quantum mechanics calculations (*cf.* ref 17).

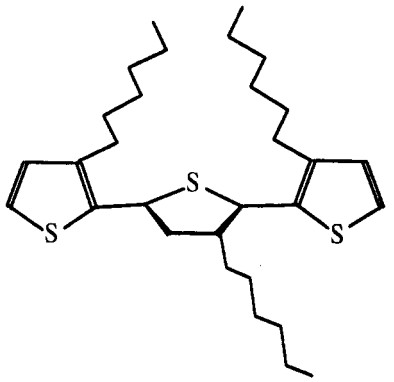


Figure 3. Preferred conformation of triad **2** (from MMP2 calculations at $\epsilon = 5$ and $\epsilon = 1.5$).

properties, ^{13}C NMR data and MMP2 calculations indicate that a triad may be considered as being the sum of two almost independent bithiophene subsystems.

A striking feature of Table 3 is that the energy difference between the two *anti-anti* conformers of the HT-HH triad, **2**, is 2 kcal mol^{-1}, while for **1**, **3**, and **4** the energy difference between the two *anti-anti* conformers is 1 order of magnitude smaller. Examination of the factors contributing to the total energy shows that this is due to the stabilization of one of the two *anti-anti* conformers of **2** by long-range van der Waals interactions. As shown in Figure 3—which gives the preferred conformation of triad **2**—the chains belonging to the terminal rings are located on the same plane and are converging, with the average H–H, C–H, and C–C distances being on the order of 3.5–5 Å. It is the sum of small and stabilizing H–H, C–H, and C–C van der Waals interactions which gives rise to the calculated energy differences between the two *anti-anti* forms for $\epsilon = 5$ as well as for $\epsilon = 1.5$. It must be stressed that the conformation reported in Figure 3 is the prevailing one (>90%) for both values of the dielectric constant, contrary to what is observed not only for **1**, **3**, and **4** but also for a series of methyl-substituted oligothiophenes.[13] Thus, **2** is an example of conformational preference dominated by long-range interactions between the alkyl chains.

The UV absorption maxima, λ_{max}, of 1–4 are reported in Table 3. All compounds have a λ_{max} value smaller than that of unsubstituted terthiophene (λ_{max} = 355 nm[5b,16]) despite the bathochromic effect which should be exerted by the alkyl groups. In consequence, as indicated by MMP2 calculations, the backbone of the four triads is not planar but tilted to a different extent as a result of the steric effects of the substituents. It should be noticed that there is a large difference (33 nm) in the λ_{max} values of the four compounds and that the λ_{max} value of triads **1** and **2**, having a HH junction, are smaller than those of triads **3** and **4**. This is accounted for by the greater inter-ring twist angle of the HH linkage compared to that of HT or TT linkages, which causes a decrease in $\pi \rightarrow \pi^*$ conjugation. For a semiquantitative check of the validity of MMP2 calculations, we have calculated the λ_{max} of 1–4 using the Pariser–Parr–Pople approach[17] and multiplying the β resonance integral bonds by $\cos^2 \omega$, where ω are the MMP2 calculated inter-ring twist angles for the prevailing conformations of 1–4. The rationale behind this procedure is that, according to Brédas *et al.*,[18] the electronic properties of oligothiophenes are well fitted by a $\cos^2$ function of the torsion inter-ring angle ω. Although the absolute values of λ_{max} calculated in this way are somewhat different (but of the same order) from experimental ones, the trend of variation on going from **1** to **4** is the same as that found experimentally. This indicates that the conformational picture of 1–4 given by MMP2 calculations for $\epsilon = 5$ is trustworthy.

Conclusions

The synthesis and the ^1H and ^{13}C NMR characterization of the four model configurational triads of poly(3-hexylthiophene) allow the unambiguous assignment of the regiochemistry, *i.e.*, of the substitution pattern, of the polymer and, in conjunction with force field MMP2 calculations, also gives information on the conformational characteristics of its different configurational segments.

The data reported in this paper show that the regiochemistry of poly(3-hexylthiophene) has a great influence on its conformational properties. Poly(3-hexylthiophene) samples containing head-to-tail linkages are characterized by the greatest conformational variability, while the presence of head-to-head linkages implies a more restricted number of conformations but larger inter-ring twist angles and conjugation interruptions. The presence of segments with adjacent head-to-tail/head-to-head linkages implies conformational stabilization through side chain interaction. These findings explain why regiochemically different versions of poly(3-hexylthiophene) display very different electrical and optical properties, as recently reported by Riecke and co-workers for a regiospecific head-to-tail and a regiorandom sample of this polymer.[7]

Experimental Section

General Procedures. *n*-Butyllithium (2.5 M in hexane), 3-bromothiophene, *N*-bromosuccinimide and tetrakis(triphenylphosphine)palladium ($Pd[(C_6H_5)P_3]_4$) were purchased from Janssen. [1,3-Bis(diphenylphosphino)propane]nickel(II) chloride ($NiCl_2$(dppp)), trimethyltin chloride, and lithium wire were purchased from Aldrich Chimica. All solvents used in reactions and chromatographies were distilled from appropriate drying agents before use. Analitical TLC was performed by using 0.25-mm silica gel plates (Merck), and visualization was accomplished by UV light. Flash chromatographies were carried out on silica gel (230–400 mesh ASTM) or reverse phase RP 18 (230–400 mesh ASTM). The mass spectra were determined using a Varian MAT 112 S mass spectrometer equipped with a Vianello s.a.s. data system. UV spectra were obtained using a Perkin-Elmer 554 spectrometer. Boiling points are uncorrected. ^1H NMR spectra were recorded at 200 MHz with a Varian VXR 200 spectrometer, using TMS (δ = 0.0 ppm) as the internal reference in $CDCl_3$ solutions. ^{13}C NMR spectra were recorded at 50 MHz with the same spectrometer, using $CDCl_3$ (δ = 77.0 ppm) as the internal reference in $CDCl_3$ solutions. ^{13}C chemical shift assignments of compounds 1–4 were made on the basis of 2D HETCOR experiments to establish proton–carbon connectivities and confirmed by HMBC and HMQC experiments.[12] Molecular mechanics MMP2 calculations were performed using the Allinger MM2(91)[19] program with a Vax Station 2000.

4,4′,3″-Tri(3-hexyl)-2,2′:5′,2″-terthiophene (1). 3-Hexylthiophene (1a). A 50-mL round-bottomed flask was charged with 5.41 g (0.23 mol) of magnesium turnings, and a solution of 33 g (0.2 mol) of 1-bromohexane in 100 mL of anhydrous ethyl ether was added under an argon atmosphere. The mixture was stirred at 0 °C (ice bath) for 30 min and then allowed to warm to room temperature. A solution of 32.6 g (0.2 mol) of 3-bromothiophene and 0.217 g (0.4 mmol) of $NiCl_2$(dppp) in 100 mL of ethyl ether was added, and the mixture was allowed to reflux for 2 h, hydrolyzed with a solution of 2 N HCl, washed with a 10% solution of $NaHCO_3$, and extracted with ether. The organic layer was washed twice with brine, dried over $MgSO_4$, and then evaporated, and 23.5 g (70%) of a 97:3 3-hexylthiophene–dodecane mixture (**1a**, by ^1H NMR analysis) was obtained, which was used without further purification. ^1H NMR (200 MHz, $CDCl_3$, ppm): 7.2 (m, 1 H); 6.9 (m, 2 H); 2.6 (t, 2 H); 1.6 (m, 2 H); 1.3 (m, 6 H); 0.9 (t, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): 143.2; 128.2; 125.0; 119.7; 31.7; 30.6; 30.3; 29.0; 22.6; 14.1.

2-Bromo-3-hexylthiophene (1b). To a solution of 6.22 g (37 mmol) of **1a** in 60 mL of 1:1 $CHCl_3$–CH_3COOH was added 6.94

g (39 mmol) of *N*-bromosuccinimide. The mixture was stirred for 30 min, and then 60 mL of distilled water was added. The mixture was first washed with a 10% KOH solution and then with water, dried over $MgSO_4$, and evaporated. After distillation (127 °C, 7 mmHg), 8.5 g (93%) of **1b** was obtained. ^1H NMR (200 MHz, $CDCl_3$, ppm): 7.1 (d, 1 H); 6.7 (d, 1 H); 2.6 (t, 2 H); 1.6 (m, 2 H); 1.3 (m, 6 H); 0.9 (t, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): 141.9; 128.2; 125.1; 108.8; 31.6; 29.7; 29.4; 28.9; 22.6; 14.1.

2-(Trimethylstannyl)-3-hexylthiophene (1c). A 100-mL round-bottomed flask was charged with 1.76 g (0.25 mol) of lithium wire and 10 mL of anhydrous THF at −10 °C, and then a solution of 5 g (25 mmol) of trimethyltin chloride in 40 mL of THF was added in two steps. The mixture was warmed to room temperature and stirred overnight. Then 8.1 mL (4.05 mmol) of this solution (0.5 M (trimethylstannyl)lithium) was added to a solution of 1 g (4.05 mmol) of 2-bromo-3-hexylthiophene at room temperature. After 30 min, the solution was quenched with ammonium chloride solution, extracted with ether, washed with brine, dried over $MgSO_4$ and evaporated. A total of 1.1 g (82%) of **1c** was obtained, which was used without further purification. ^1H NMR (200 MHz, $CDCl_3$, ppm): 7.50 (d, 1 H); 7.08 (d, 1 H); 2.6 (m, 2 H); 1.6 (m 2 H); 1.3 (m, 6 H); 0.9 (t, 3 H); 0.4 (s, 9 H). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): 150.8; 131.2; 130.4; 129.3; 32.6; 32.1; 31.8; 29.3; 22.6; 14.1; −8.0.

3,3′-Di(3-hexyl)-2,2′-bithiophene (1d). A solution of 0.457 g (1.85 mmol) of 2-bromo-3-hexylthiophene in 30 mL of freshly distilled toluene was added to a solution of 0.612 g (1.85 mmol) of 3-hexyl-2-(trimethylstannyl)thiophene in 30 mL of toluene containing 21 mg (0.018 mmol) of $[(C_6H_5)_3P]_4Pd$. The mixture was allowed to reflux and its evolution followed by TLC analysis. After complete disappearance of 3-hexyl-2-(trimethylstannyl)-thiophene, the brownish solution was hydrolized with ice cold 2 N HCl, neutralized with $NaHCO_3$, and extracted with ether. The organic layer was washed twice with brine, dried over $MgSO_4$, and then evaporated. The residue was purified by flash chromatography (silica gel RP 18/85:15 CH_3OH:CH_2Cl_2), and 0.36 g (59%) of **1d** as a colorless oil was obtained. MS, *m/e* 334 ($M^{\bullet+}$). ^1H NMR (200 MHz, $CDCl_3$, ppm): 7.25 (d, 2 H); 6.94 (d, 2 H); 2.5 (m, 4 H); 1.5 (m, 4 H); 1.2 (m, 12 H); 0.8 (m, 6 H). ^{13}C NMR (50 MHz $CDCl_3$, ppm): 142.3; 128.7; 128.4; 125.2; 31.7; 30.7; 29.1; 28.8; 22.6; 14.1.

3,3′-Di(3-hexyl)-5-bromo-2,2′-bithiophene (1e). To a solution of 1.1 g (3.3 mmol) of 3,3′-di(3-hexyl)-2,2′-bithiophene in 60 mL of 1:1 $CHCl_3$:CH_3COOH was added 0.62 g (3.5 mmol) of *N*-bromosuccinimide. The mixture was stirred for 30 min, and then 60 mL of distilled water was added. The mixture was first washed with a 10% KOH solution and then with water, dried over $MgSO_4$, and evaporated. After flash chromatography (silica gel, hexane), 1.04 g (2.5 mmol, 76%) of **1e** was obtained as a yellow oil. ^1H NMR (200 MHz, $CDCl_3$, ppm): 7.26 (d, 1 H); 6.93 (d, 1 H); 6.90 (s, 1 H); 2.5 (m, 4 H); 1.5 (m, 4 H); 1.3 (m, 12 H); 0.8 (m, 6 H). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): 143.2; 142.9; 131.3; 130.3; 128.6; 127.4; 125.8; 111.7; 32.0; 31.7; 31.6; 30.7; 30.5; 29.7; 29.4; 29.1; 29.0; 28.8; 28.7; 22.7; 22.6; 22.5; 14.1; 14.0.

3-Hexyl-5-(trimethylstannyl)thiophene (1f). To a solution of 3.36 g (20 mmol) of 3-hexylthiophene in 100 mL of ethyl ether containing 2.55 g (22 mmol) of *N,N,N′,N′*-tetramethylethylendiamine was added 8.8 mL (22 mmol) of BuLi (2.5 M in hexane). The mixture was allowed to reflux for 1 h and then cooled to 0 °C (ice bath), and a solution of 4.38 g (22 mmol) of trimethyltin chloride in 20 mL of ethyl ether was added. The mixture was allowed to warm to room temperature, quenched with ammonium chloride solution, washed with brine, dried over Na_2SO_4, and evaporated, and 5.9 g (90%) of **1f** was obtained, which was used without further purification. ^1H NMR (200 MHz, $CDCl_3$, ppm): 7.18 (m, 1 H); 7.0 (d, 1 H); 2.6 (m, 2 H); 1.6 (m, 2 H); 1.3 (m, 6 H); 0.9 (t, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): 144.5; 137.1; 136.6; 125.7; 31.7; 30.7; 30.0; 29.2; 22.6; 14.1.

4,4′,3″-Tri(3-hexyl)-2,2′:5′,2″-terthiophene (1). To a solution of 0.48 g (1.45 mmol) of 3-hexyl-5-(trimethylstannyl)-thiophene and 17 mg (0.0015 mmol) of $Pd[(C_6H_5)_3P]_4$ in 30 mL of toluene was added a solution of 0.6 g (1.45 mmol) of 3,3′-di-(3-hexyl)-5-bromo-2,2′-bithiophene in 30 mL of toluene. The mixture was allowed to reflux for 4 h, hydrolyzed with 2 N HCl, neutralized with a 10% solution of $NaHCO_3$, washed twice with brine, dried over $MgSO_4$, and evaporated. Flash chromatography with RP 18 silica gel and 8:2 CH_3OH:CH_2Cl_2 as the eluent gave 0.37 g (51%) of **1** as a pale yellow oil. MS, *m/e* 500 ($M^{\bullet+}$); λ_{max} ($CHCl_3$): 326 nm. ^1H NMR (200 MHz, $CDCl_3$, ppm): 7.27 (d, 1 H); 7.0 (s, 1 H); 6.99 (d, 1 H); 6.95 (d, 1 H); 6.77 (m, 1 H); 2.5 (m, 6 H); 1.5 (m, 6 H); 1.3 (m, 18 H); 0.9 (m, 9 H). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): 144.1; 143.1; 142.5; 137.3; 137.1; 128.6; 128.4; 127.6; 125.4; 124.8; 118.8; 31.7; 30.7; 30.6; 30.5; 30.4; 29.1; 29.0; 28.9; 22.6; 14.1.

3,4′,3″-Tri(3-hexyl)-2,2′:5′,2″-terthiophene (2). 2,5-Dibromo-3-hexylthiophene (2a). To a solution of 5.04 g (30 mmol) of **1a** in 120 mL of 1:1 $CHCl_3$:CH_3COOH was added 11.24 g (63 mmol) of *N*-bromosuccinimide. The mixture was stirred for 30 min, and then 120 mL of distilled water was added. The mixture was first washed with a 10% KOH solution and then with water, dried over $MgSO_4$, and evaporated. After flash chromatography (silica gel, hexane), 6.94 g (71%) of **2a** was obtained as a yellow oil. ^1H NMR (200 MHz, $CDCl_3$, ppm): 6.76 (s, 1 H); 2.49 (t, 2 H); 1.5 (m, 2 H); 1.3 (m, 6 H); 0.88 (t, 3 H). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): 143.0; 131.0; 110.3; 107.9; 31.6; 29.5; 29.4; 28.8; 22.6; 14.0.

3,4′,3″-Tri(3-hexyl)-2,2′:5′,2″-terthiophene (2). To a solution of 0.582 g (1.76 mmol) of 2-(trimethylstannyl)-3-hexylthiophene in 30 mL of toluene was added a solution of 0.287 g (0.88 mmol) of 2,5-dibromo-3-hexylthiophene in 30 mL of toluene containing also 10 mg (0.009 mmol) of $Pd[(C_6H_5)_3]_4$. The mixture was allowed to reflux for 4 h, hydrolyzed with 2 N HCl, neutralized with a 10% solution of $NaHCO_3$, washed twice with brine, dried over $MgSO_4$, and evaporated. Flash chromatography with RP 18 silica gel and 8:2 CH_3OH:CH_2Cl_2 as the eluent gave 0.11 g (0.2 mmol, 24%) of **2** as a pale yellow oil. MS, *m/e* 500 ($M^{\bullet+}$); λ_{max} ($CHCl_3$): 315 nm. ^1H NMR (200 MHz, $CDCl_3$, ppm): 7.30 (d, 1 H); 7.15 (d, 1 H); 6.98 (s, 1 H); 6.95 (d, 1 H); 6.93 (d, 1 H); 2.8 (m, 2 H); 2.5 (m, 4 H); 1.6 (m, 6 H); 1.3 (m, 18 H); 0.9 (m, 9 H). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): 142.6; 142.5; 139.4; 135.9; 130.9; 130.0; 128.6; 128.5; 127.3; 125.5; 123.4; 31.7; 30.8; 30.7; 30.6; 29.3; 29.2; 29.1; 28.9; 22.6; 14.1.

4,4′,4″-Tri(3-hexyl)-2,2′:5′,2″-terthiophene (3). To a solution of 0.49 g (1.51 mmol) of 2,5-dibromo-3-hexylthiophene in 50 mL of toluene was added a solution of 1 g (3 mmol) of 3-hexyl-5-(trimethylstannyl)thiophene and 17 mg (0.015 mmol) of $Pd[(C_6H_5)_3P]_4$. The mixture was allowed to reflux for 4 h, hydrolyzed with 2 N HCl, neutralized with a 10% solution of $NaHCO_3$, washed twice with brine, dried over $MgSO_4$, and evaporated. Flash chromatography with RP 18 silica gel and 8:2 CH_3OH:CH_2Cl_2 as the eluent gave 0.2 g (27%) of **3** as a pale yellow oil. MS, *m/e* 500 ($M^{\bullet+}$); λ_{max} ($CHCl_3$): 348 nm. ^1H NMR (200 MHz, $CDCl_3$, ppm): 7.00 (d, 1 H); 6.96 (s, 1 H); 6.94 (d, 1 H); 6.86 (1 H); 6.76 (1 H); 2.7 (m, 2 H); 2.5 (m, 4 H); 1.6 (m, 6 H); 1.3 (m, 18 H); 0.9 (m, 9 H). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): 144.1; 143.6; 139.9; 136.9; 135.7; 135.2; 129.8; 127.1; 126.2; 124.8; 119.9; 118.9; 31.7; 30.5; 30.4; 30.3; 29.4; 29.2; 29.0; 22.6; 14.1.

3,4′,4″-Tri(3-hexyl)-2,2′:5′,2″-terthiophene **(4). 3,4′-Di(3-hexyl)-2,2′-bithiophene (4a).** A solution of 2-bromo-3-hexylthiophene (2 g, 8 mmol) in 30 mL of toluene was added to a solution of 3-hexyl-5-(trimethylstannyl)thiophene (2.65 g, 8 mmol) in 50 mL of toluene containing 92 mg (0.08 mmol) of $Pd[(C_6H_5)_3P]_4$. The mixture was allowed to reflux for 20 h and then hydrolyzed with ice cold 2 N HCl, neutralized with $NaHCO_3$, and extracted with ether. The organic layer was washed twice with brine, dried over $MgSO_4$, and then evaporated. Flash chromatography (silica gel RP 18/90:10 CH_3OH:CH_2Cl_2) gave 0.61 g (23%) of **4a** as a pale yellow oil. MS *m/e* 334 ($M^{\bullet+}$). ^1H NMR (200 MHz, $CDCl_3$, ppm): 7.10 (d, 1 H); 6.93 (d, 1 H); 6.88 (d, 1 H); 6.85 (m, 1 H); 2.7 (m, 2 H); 2.5 (m, 2 H); 1.6 (m, 4 H); 1.3 (m, 12 H); 0.9 (m, 6 H). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): 143.5; 139.3; 135.9; 131.0; 129.6; 127.3; 123.4; 119.9; 31.7; 31.6; 30.7; 30.5; 30.4; 29.2; 29.1; 29.0; 22.5; 14.1.

3,4′-Di(3-hexyl)-5-bromo-2,2′-bithiophene (4b). To a solution of 0.5 g (1.5 mmol) of 3,4′-di(3-hexyl)-2,2′-bithiophene in 40 mL of $CHCl_3$ at 0 °C (ice bath) was added 0.266 g (1.5 mmol) of *N*-bromosuccinimide. The mixture was stirred for 30 min, and then 40 mL of distilled water was added. The mixture was first washed with a 10% KOH solution and then with water, dried over $MgSO_4$, and evaporated. After flash chromatography (silica gel, hexane), 0.607 g (98%) of **4b** was obtained as a pale yellow oil. ^1H NMR (200 MHz, $CDCl_3$, ppm): 7.12 (d, 1 H); 6.89 (d, 1

H); 6.78 (s, 1 H); 2.7 (m, 2 H); 2.5 (m, 2 H); 1.6 (m, 4 H); 1.3 (m, 12 H); 0.9 (m, 6 H). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): 142.3; 139.9; 135.7; 130.0; 129.9; 126.9; 125.8; 108.5; 31.6; 30.7; 29.7; 29.6; 29.2; 29.1; 28.9; 22.0; 14.1.

3,4′,4″-Tri(3-hexyl)-2,2′:5′,2″-terthiophene (4). To a solution of 0.48 g (1.45 mmol) of 3-hexyl-5-(trimethylstannyl)-thiophene and 17 mg (0.015 mmol) of $Pd[(C_6H_5)_3P]_4$ in 30 mL of toluene was added a solution of 0.6 g (1.45 mmol) of 3,4′-di-(3-hexyl)-5-bromo-2,2′-bithiophene in 30 mL of toluene. The mixture was allowed to reflux for 4 h, hydrolyzed with 2 N HCl, neutralized with a 10% solution of $NaHCO_3$, washed twice with brine, dried over $MgSO_4$, and evaporated. Flash chromatography with RP 18 silica gel and 8:2 CH_3OH:CH_2Cl_2 as the eluent gave 0.48 g (69%) of **4** as a pale yellow oil. MS, *m/e* 500 ($M^{\bullet+}$); λ_{max} ($CHCl_3$): 336 nm. ^1H NMR (200 MHz, $CDCl_3$, ppm): 7.12 (d, 1 H); 6.96 (d, 1 H); 6.92 (s, 1 H); 6.90 (d, 1 H); 6.87 (m, 1 H); 2.7 (m, 4 H); 2.6 (m, 2 H); 1.6 (m, 6 H); 1.5 (m, 18 H); 0.9 (m, 9 H). ^{13}C NMR (50 MHz, $CDCl_3$, ppm): 143.6; 139.5; 135.6; 133.9; 130.7; 130.0; 128.6; 127.1; 123.5; 120.0; 31.7; 30.7; 30.6; 30.5; 30.4; 29.3; 29.2; 29.0; 22.6; 14.1.

Poly(3-hexylthiophene). Poly(3-hexylthiophene) was prepared by chemical polymerization of 3-hexylthiophene (1g, 0.006 mol, in 40 mL of $CHCl_3$) with dry $FeCl_3$ (3.87 g, 0.024 mol, in suspension in 100 mL of $CHCl_3$) according to the modalities described in ref 10. The reaction mixture was stirred overnight at room temperature and then worked up with MeOH, and the polymer was extracted with a Soxhlet apparatus using methanol (1 night) and acetone (1 night). The black solid was dried under vacuum and then repeatedly washed using a hydrazine solution (2% w/w in water). Then the aqueous phase was filtered, and the solid was dissolved in THF and precipitated again using MeOH. The yield was 45%. λ_{max} ($CHCl_3$): 437 nm. ^{13}C NMR ($CDCl_3$, TMS, ppm): 139.8; 133.8; 130.5; 128.7; 32.0; 30.5; 29.3; 22.5; 14.2.

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