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Published on Web 04/05/2006

Chiral Amphiphilic Self-Assembled α,α′-Linked Quinque-, Sexi-, and Septithiophenes: Synthesis, Stability and Odd−Even Effects

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Abstract: The synthesis, characterization, and self-assembly in butanol of a series of well-defined α,α′-linked quinqui-, sexi-, and septithiophenes substituted, via ester links at their termini, by chiral oligo(ethylene oxide) chains carrying an α, β, δ, and ϵ methyl, respectively, are reported. Studies of the self-assembly of these molecules using UV/visible absorption, luminescence, and circular dichroism spectroscopies reveal, for the sexithiophene case, that the magnitude of the observed Cotton effect in the aggregates diminishes progressively as the chiral substituent is moved away from the thiophene segment. The stability of the assemblies increases with the length of the oligothiophene and as the substituent chiral unit is moved away from the aromatic core, being greatest for the unsubstituted case. The sign of the Cotton effect alternates in an "odd/even" manner as the position of the chiral substituent is moved along the oligo(ethylene oxide) chain and on going from the quinquethiophene to the septithiophene having the same side chain. Atomic force microscopy on materials deposited from solution on an aluminum or glass surface and optical measurements show that capsules are formed from the oligothiophenes with H-type packing of the aromatic segments.

Introduction

Chiroptical techniques, such as circular dichroism (CD), are commonly used to probe the secondary and tertiary structures in biopolymers[1] and have recently become a highly sensitive tool for investigating the degree of helical order and stability in π-conjugated polymer assemblies.[2] Chiroptical properties of these assemblies are associated with an exciton coupled CD effect,[1] and model compounds have been used to investigate the angle between the π-conjugated segments in the helical aggregates.[3] Aggregation-induced Cotton effects have been reported for chiral π-conjugated polymers and their related oligomers.[2] The helicity and stability of such assemblies are important for any putative application since the details of organization will influence the macroscopic properties of the final supramolecular materials.[2]

We report here a systematic study of the stability and chiral aggregation in butanol of a set of α,α′-substituted oligothiophenes as a function of oligomer length and position of chiral substituent in the side chain. Previously, we have studied polythiophenes substituted with chiral side chains and found that the helical packing is dependent on both the absolute configuration of the stereocenter and its distance from the rigid core.[4] Now, we have synthesized α,α′-linked oligothiophenes with five, six, or seven thiophene rings, with penta(ethyleneoxide) substituents attached via ester links at the terminal α-positions (Chart 1) and carrying a stereocenter at four different locations on the substituent.[5] The self-assembly process shows odd−even effects, as revealed by the sign of the Cotton effect in the aggregates, with respect to both the position of the chiral substituent and the length of the oligomer sequence. Odd−even effects have initially been reported for liquid crystals[6] and afterward for polymers having mesogenic substituents.[7] Recently such effects have been found for a variety of self-assembled

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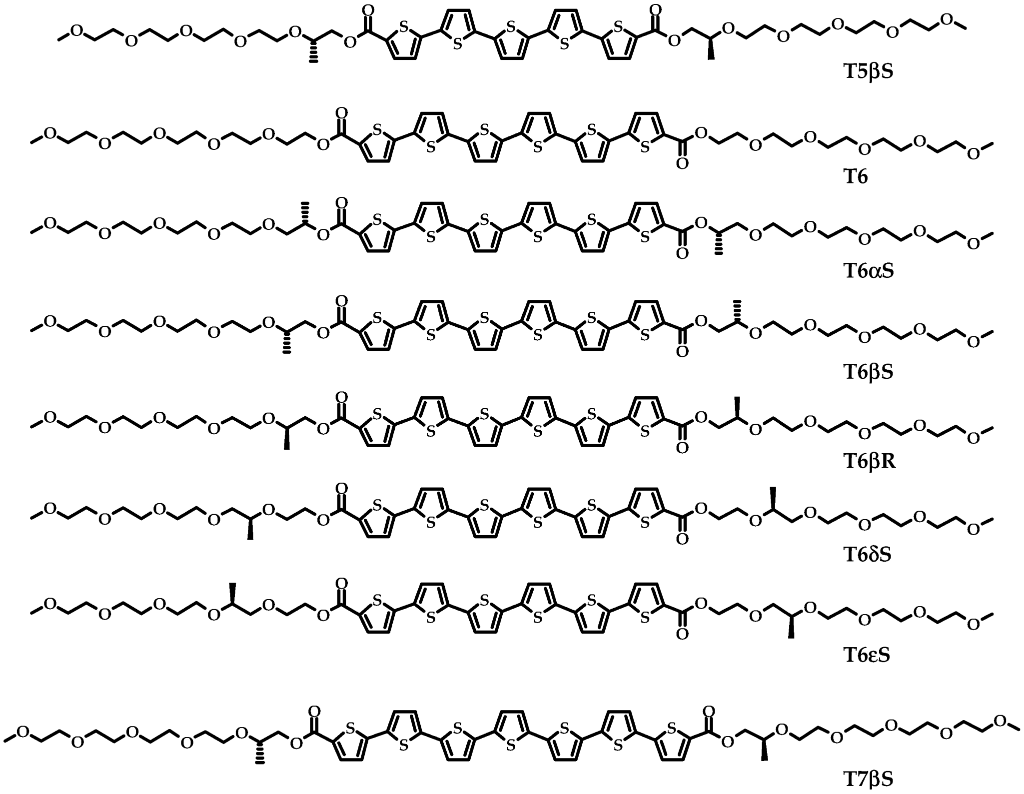
10.1021/ja0607234 CCC: $33.50 © 2006 American Chemical Society

Chart 1. Chiral Oligothiophenes Used in This Study; for Codes See Text



systems;[8] however, for π-conjugated systems odd−even effects have been seldom observed.[4,9] The stability of the assembly increases with the length of the oligothiophene sequence and as the chiral unit is moved away from the aromatic core, being largest for the unsubstituted case. Under the conditions adopted in this study the oligomers primarily form hollow capsules in solution,[10] presumably being present as self-assembled chiral domains in the shell of the macroscopic capsules. In earlier studies of these systems, rodlike helical assemblies and flat "crêpes" have been generated on a silicon surface by slow evaporation of THF solutions;[11] it is becoming clear that the exact course of self-assembly in these systems is a sensitive function of the experimental protocol adopted (solvent, substrate, rate of formation, temperature, and deposition method).

Results and Discussion

Synthesis. A series of chirally substituted (ethylene oxide)s were prepared and used to derivatize oligothiophenes at their terminal α-positions. A simple code has been adopted for identifying the chiral molecules discussed, consisting of an Arabic numeral followed by a Greek letter plus either **S** or **R**. All the chiral molecules considered have a structural motif (Figure 1)

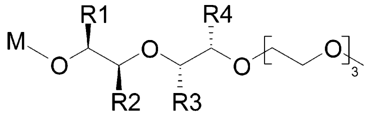


Figure 1. Structural motif for S-chiral molecules.

in which the unit M is identified by a number and the substituents R1−R4 are always one methyl and three hydrogen atoms. When the methyl substituent is at R1 it is identified by the letter α, at R2 by β, at R3 by δ, and at R4 by ϵ; R or S identifies the chirality at the methyl substituted carbon. The target molecules were the substituted α,α′-linked quinque-, sexi-, and septithiophenes, and these are identified as T5, T6, and T7, respectively.

Schemes 1 and 2 show the route adopted for the synthesis of the chiral alcohols **11αS**, **11βS**, **11δS**, and **11ϵS** starting from **3S** and **4S**. The latter molecules are made from ethyl (*S*)-(−)-lactate (purity of 98%) and methyl (*R*)-(+)-lactate (98% pure with an ee of $>$96%), respectively.[11] The ee value of ethyl (*S*)-(−)-lactate was determined by gas chromatography (GC) on a capillary column with a permethylated β-cyclodextrin stationary phase yielding an ee $>$ 99.5%.[12] Part of this synthetic route is based on earlier work that also showed the fidelity of keeping the enantiomeric excess as high as that of the starting materials.[13] The chiral alcohol **11βR** is not shown in the schemes but was synthesized in an analogous way to that described previously

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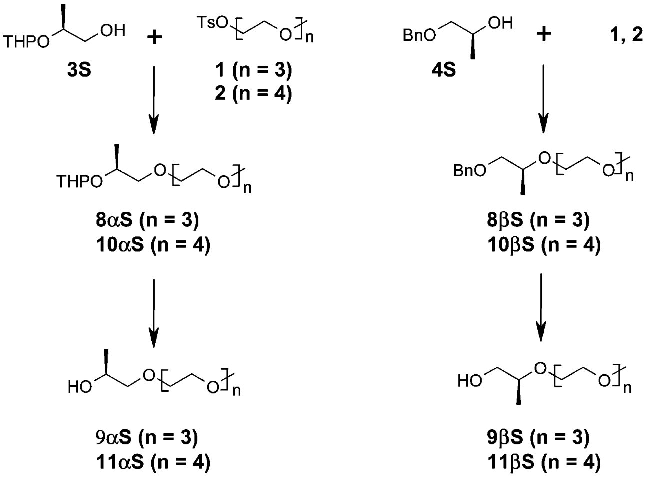
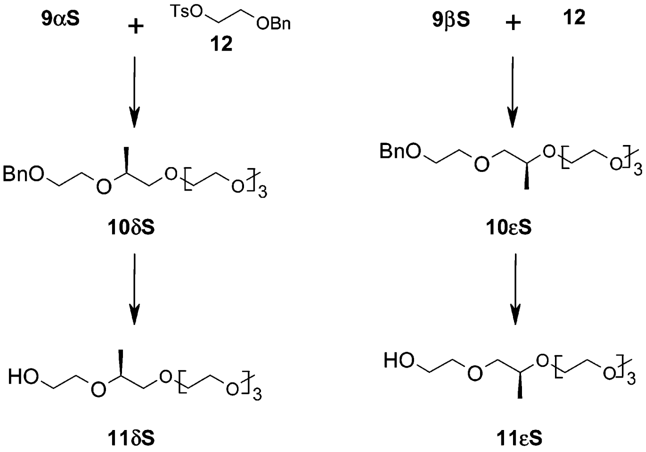
Scheme 1. Synthesis of the **S**-Enantiomers of the Oligo(ethylene oxide) **9αS**, **9βS**, **11αS**, and **11βS**



Scheme 2. Synthesis of the **S**-Enantiomers of the Oligo(ethylene oxide) **11δS** and **11εS**



for the alcohol **11βS**.[5,14] Base-catalyzed reactions of the tosylated tetraethylene oxide **2** with the monoprotected chiral glycol derivatives **3S** and **4S** followed by cleavage of the THP or benzyl protecting group gave the alcohols **11αS** and **11βS**, respectively. The shorter molecules **9αS** and **9βS** were obtained using the tosylated tri(ethylene glycol) **1** and the analogous sequence of reactions (Scheme 1).

Reaction of **9αS** and **9βS** with the tosylated achiral benzyl protected glycol **12** and cleavage of the benzyl protecting group gave the alcohols **11δS** and **11εS** (Scheme 2).

The synthesis route for the target molecules **T5βS**, **T6αS**, **T6βS**, **T6δS**, **T6εS**, and **T7βS** is shown in Scheme 3. The respective enantiomeric compounds **T5βR**, **T6βR**, and **T7βR** are not shown but were synthesized in an analogous way.[14] Reaction of the chiral alcohols **11αS**, **11βS**, **11δS**, and **11εS** with 2-bromothiophene-5-carbonyl chloride **13** using pyridine as base gave the esters **14αS**, **14βS**, **14δS**, and **14εS**, respectively. Following the strategy published in our previous work,[5] the required oligothiophene units were formed by a Stille cross-coupling reaction in the last step of the synthesis. The red crude products obtained were readily soluble in chloroform and were purified by repeated reprecipitation and size exclusion chromatography using BioBeads.[14]

All the key compounds, **T5βS**, **T6**, **T6αS**, **T6βS**, **T6δS**, **T6εS**, **T7βS**, **T5βR**, **T6βR**, and **T7βR**, used in the subsequent studies were characterized via correct elemental and ^{1}H NMR and ^{13}C NMR analyses and appropriate spectroscopic properties.[14] Also the sequences used are known to yield nonracemized products.[13] However, using MALDI-TOF MS and high-temperature GPC, we established that there were trace amounts of impurities in some compounds.[14] Thus, some had traces of the compound in question with one EO unit less than required, which arises from the difficulty in obtaining a perfect separation of the homologues **9αS**/**11δS** and **9βS**/**11εS** (see Scheme 2), and some had additional thiophene residues in the aromatic core, arising from the well-documented multiple coupling side reactions associated with Stille coupling.[15] The estimated purities of the samples are all well above 96%. The trace impurities did not influence the self-assembly behavior of interest here since a self-consistent argument describes the whole set of compounds irrespective of whether trace impurities were detected; nevertheless it seems proper to record their existence since it may be relevant in future extensions of this work.

Self-Assembly in Solution. The UV/vis absorption spectrum of **T5βS** in tetrahydrofuran (THF) shows a maximum at $\lambda = 433$ nm. For all **T6** derivatives, this maximum is located at $\lambda = 435$ nm, while, for **T7βS**, it occurs at $\lambda = 447$ nm. In the fluorescence spectra, maxima are found at $\lambda = 511$, 530, and 548 nm for **T5βS**, all **T6** derivatives, and **T7βS**, respectively. The position of the maximum depends on the conjugation length, and the shape of the spectra are similar to those reported earlier for molecularly dissolved α,α′-terminally disubstituted oligothiophenes.[16] The self-assembly of the oligothiophenes was studied in butanol. A solution of **T5βS** in butanol at 300 K shows a UV/vis spectrum similar to that recorded in THF, and the absorption maximum is located at $\lambda = 438$ nm (Figure 2a). Upon cooling to 213 K, this band shifts to the blue by 63 nm, $\lambda = 375$ nm, indicating H-type aggregation. For the **T6** derivatives, the shift upon cooling depends on the position of the stereocenter. The smallest blue shift is observed for **T6αS** (37 nm), while **T6βS** shifts by 52 nm, **T6δS** shifts by 62 nm, and **T6εS** shifts by 65 nm (Figure 2c). The largest shift (69 nm) was observed for **T6a** indicating that the sexithiophenes, lacking the methyl group of the stereocenter, show a stronger exciton coupling probably as a result of a better packing (vide infra). For **T7βS** in butanol, a similar blue shift from $\lambda = 450$ nm at 343 K to $\lambda = 410$ nm at 273 K is found (Figure 2d). Hence, it is now clear why absorption data reported in the literature for similar aggregated oligothiophenes can change from derivative to derivative depending on a very subtle difference in the side chain.[17]

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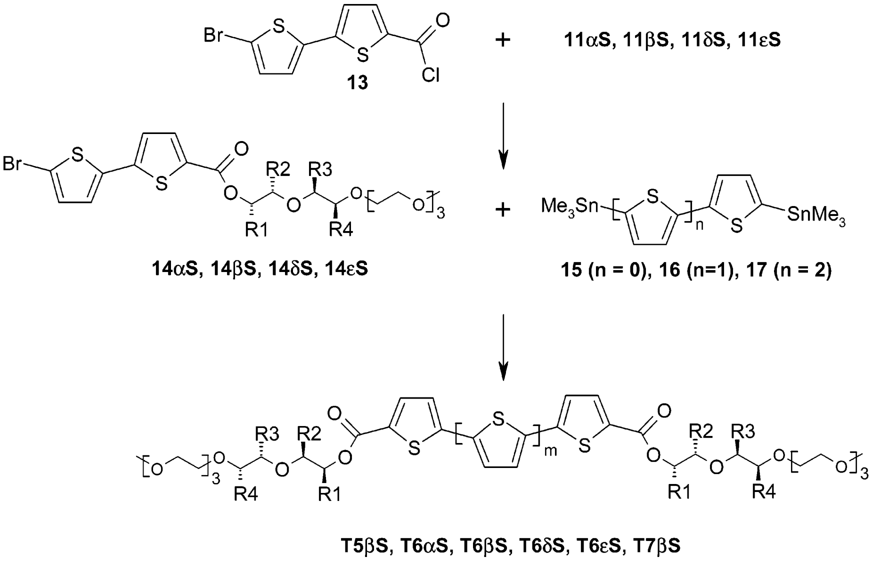
Scheme 3. Synthesis of the **S**-Enantiomers of the Oligothiophenes **T5βS**, **T6αS**, **T6βS**, **T6δS**, **T6εS**, and **T7βS**[a]



[a] Where for α**S** R1 = CH_3, R2, R3, R4 = H; for β**S** R2 = CH_3, R1, R3, R4 = H; for δ**S** R3 = CH_3, R1, R2, R4 = H; and for ε**S** R4 = CH_3, R1, R2, R3 = H. For **T5βS** m = 3; for **T6αS**, **T6βS**, **T6δS**, and **T6εS** m = 4; and for **T7βS** m = 5.

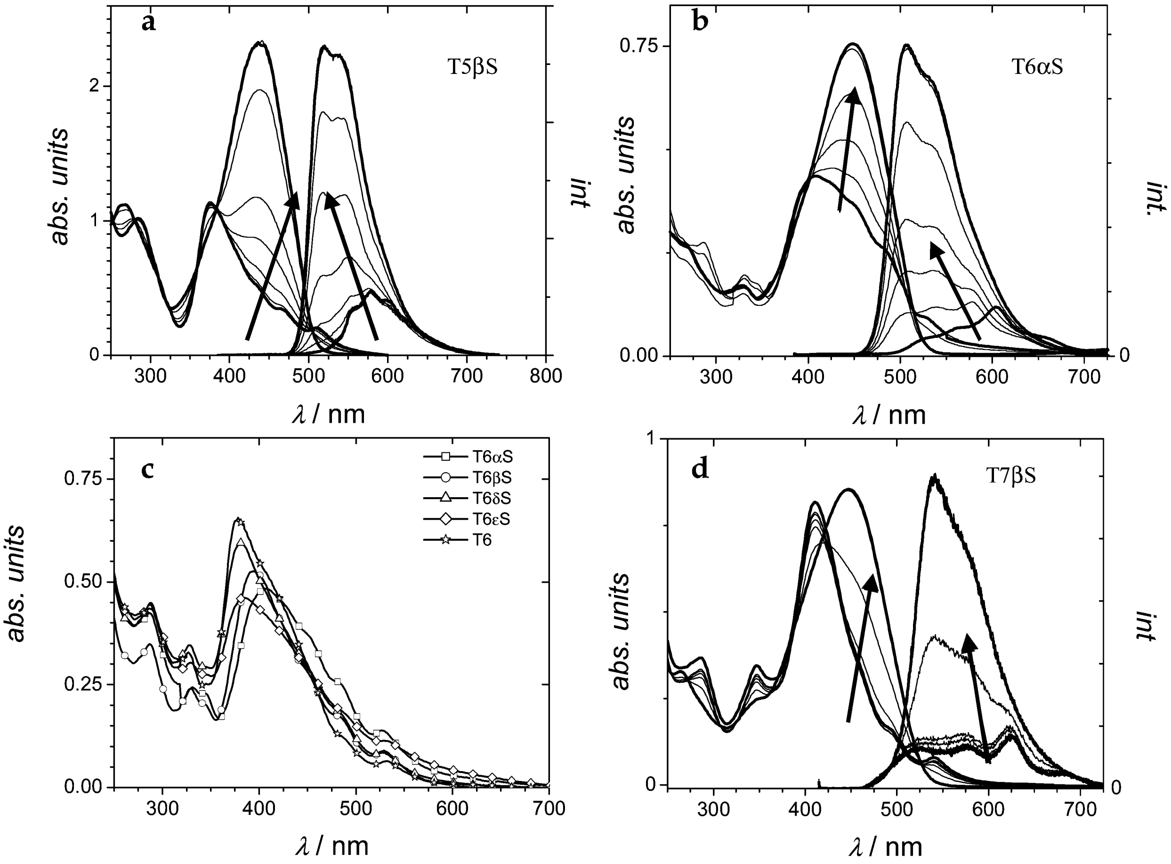


Figure 2. Temperature-dependent UV/vis and emission spectra in butanol (2.6 × 10^{-5} M) for (a) **T5βS**, (b) **T6αS**, and (d) **T7βS**. UV/vis spectra at 283 K are plotted for all **T6** derivatives in (c). The direction of the arrows indicates an increase in temperature (see text).

The fluorescence intensity of solutions of **T5βS** in butanol at 213 K was reduced when compared to that found at 300 K, and the maximum was red shifted to λ = 579 nm, typical for H-aggregates (Figure 2a). All **T6** derivatives show an emission maximum at λ = 610 nm below 300 K, while above 370 K, a much more intense emission is found having a maximum at λ = 508 nm (Figure 2b). In the case of **T7βS**, a similar red shift and quenching of the emission are observed on going from λ = 540 nm at 343 K to λ = 625 nm at 273 K (Figure 2d).

Odd−Even Effects in Chiral Packing. For **T5βS**, a bisignate Cotton effect is found at 213 K, while at 300 K no Cotton effect exists. The Cotton effect shows a positive sign at lower energy ($\lambda_{[+]}$ = 407 nm) and a negative Cotton effect at higher energy ($\lambda_{[-]}$ = 347 nm) revealing a right-handed helical packing (Figure

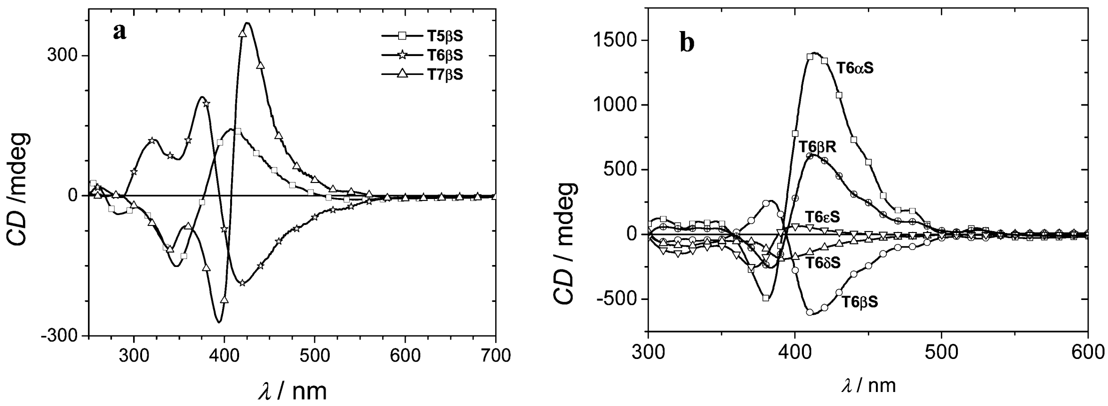


Figure 3. (a) CD spectra of **T5βS**, **T6βS**, and **T7βS** in butanol (2.6×10^{-5} M) at 283 K. (b) CD spectra for all chiral **T6** derivatives (8×10^{-5} M) at 283 K.

3). The zero-crossing at the absorption maximum of the chromophore absorption indicates exciton coupling as a result of chiral aggregation.[1] The sign of the Cotton effect of **T5βS** is opposite to that observed for the corresponding **T6βS** aggregates ($\lambda_{[-]} = 419$ nm and $\lambda_{[+]} = 375$ nm, left-handed helicity) but similar to that found for the aggregates of **T7βS** ($\lambda_{[+]} = 425$ nm and $\lambda_{[-]} = 394$ nm, right-handed helicity) (Figure 3a). Remarkably, the behavior is different from T4, T5, T6 organogelators bearing similar cholesteric side chains that did not show an alternation of the sign of the Cotton effect.[17] As expected, the sign of the Cotton effect is reversed for aggregates of **T6βR** compared to **T6βS** (Figure 3b) having a stereocenter with the opposite configuration. The sign of the Cotton effect also depends on the position of the stereocenter in the substituent (Figure 3b). For odd-numbered positions, i.e. **T6αS** and **T6ϵS**, the low energy side has a positive sign, while the even numbered, i.e., **T6βS** and **T6δS**, have a negative sign. Interestingly, the magnitude of the Cotton effect decreases upon moving the stereocenter away from the chromophore, as seen when comparing **T6ϵS** with **T6αS** and **T6δS** with **T6βS**. In addition, the intensity of the Cotton effect increases upon extending the conjugation length, and remarkably, the sign also depends on the number of thiophene rings; compare **T5βS**, **T6βS**, and **T7βS** (Figure 3a). The observed odd−even effects in the optical activity of the sexithiophene assemblies are similar to those reported earlier for β-substituted polythiophenes[4] and are in agreement with the established ROD-REL rules for cholesteric liquid crystals and helical polymers.[6,7]

Stability of Aggregates. When the UV/vis maxima for all **T6** derivatives at the same concentration are plotted versus temperature, the phase-transition curves shift to higher temperatures (Figure 4) as the stereocenter is moved further away from the thiophene segment. The T_m of the thiophene stacks, as recorded by cooling a sample at a rate of 10 K/h, is located at 288 K (**T6αS**), 316 K (**T6βS**), 323 K (**T6δS**), 328 K (**T6ϵS**), and 330 K (**T6**) showing that the achiral stacks are the most stable. The enthalpy gain computed from the slope of the curves (Figure 4a) is lowest for **T6αS** (−11 kJ/mol) and highest for **T6** (−28 kJ/mol). The differences in the transition curves reflect a better packing of the T6 segments when the steric hindrance of the stereocenter in the side chains is removed. This behavior indicates that the preferred orientation is similar to that found for oligothiophenes in the solid state in which the angle between the long axis of adjacent oligothiophenes is close to zero.[16] In the case of methyl substitution, this group sterically hinders an angle of 0°. As a result, both the position of the stereocenter on the side chain and the conjugation length of oligothiophenes determine the stability of the stacks (Figure 4b). Thus, the observation that more $\pi-\pi$ interactions enhance the stability of the stacks, as indicated by the change of the Cotton effect intensity in aggregates obtained upon cooling solutions of **T5βS**, **T6βS**, and **T7βS**, is similar to earlier conclusions from studies of a series of oligothiophene organogelators[17] and stacked oligo(*p*-phenylenevinylene)s.[18]

Molecular Modeling. We have modeled the assembly of the oligothiophenes (starting from **T7βS**), with a combination of density functional theory calculations (for the internal structure of the molecules) and force-field molecular mechanics and molecular dynamics (MD) simulations (for the structure of stacks). To take into account both the lateral and the in-stack intermolecular interactions, the model system studied consisted of two parallel columns of eight molecules of **T7βS**. MD simulations[14] reveal two stable structures corresponding to right- and left-handed helices. The molecules within a stack are not in perfect registry (i.e., they are slightly shifted and rotated) with respect to each other, while the planes of the T7 segments remain parallel to each other. As a result, the molecular organization within the stacks, seen from the side of a single column in Figure 5, clearly shows a helical character. The mean distance between the π-systems of adjacent molecules is 3.7 ± 0.5 Å, which is typical of π-stacked oligothiophenes.[16] The difference in the energy calculated for the left- and right-handed assemblies is 200 kJ/mol in favor of the right-handed assembly. No interconversion occurs between the two structures during the 800 ps of the simulation at 300 K. This is in agreement with the experimental results: aggregates of **T7βS** display a positive Cotton coupling (Figure 3a), which is the signature of right-handed helicity.[1] The methyl groups at the chiral centers uniformly point upward (downward) in the groups on the left (right) side of the stack. The steric hindrance of the methyl groups at the chiral centers probably induces the longitudinal shift and rotation of the molecules in the stacks, giving rise to the helical structure. The angle measured between the long axis of neighbor molecules in the stack is 7 ± 1° and is similar for both left- and right-handed assemblies. Based on this angle, a full turn would require about 50 molecules, which would

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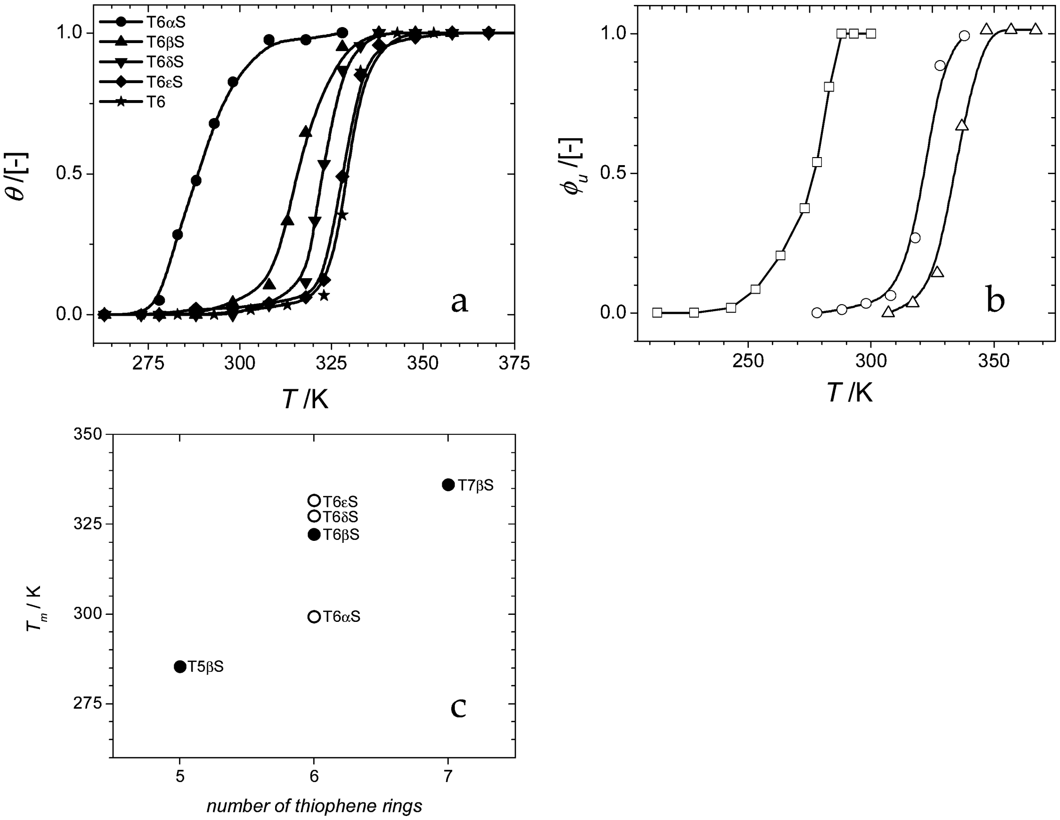

Figure 4. (a) Phase transition curves of **T6** derivatives at 2.6 × 10^{-5} M in butanol based on UV/vis data. (b) Phase transition curves of **T5**β**S** (□), **T6**β**S** (○), and **T7**β**S** (△) at 2.6 × 10^{-5} M in butanol based on CD data. (c) Melting temperature T_m versus number of thiophene rings and substitution pattern.

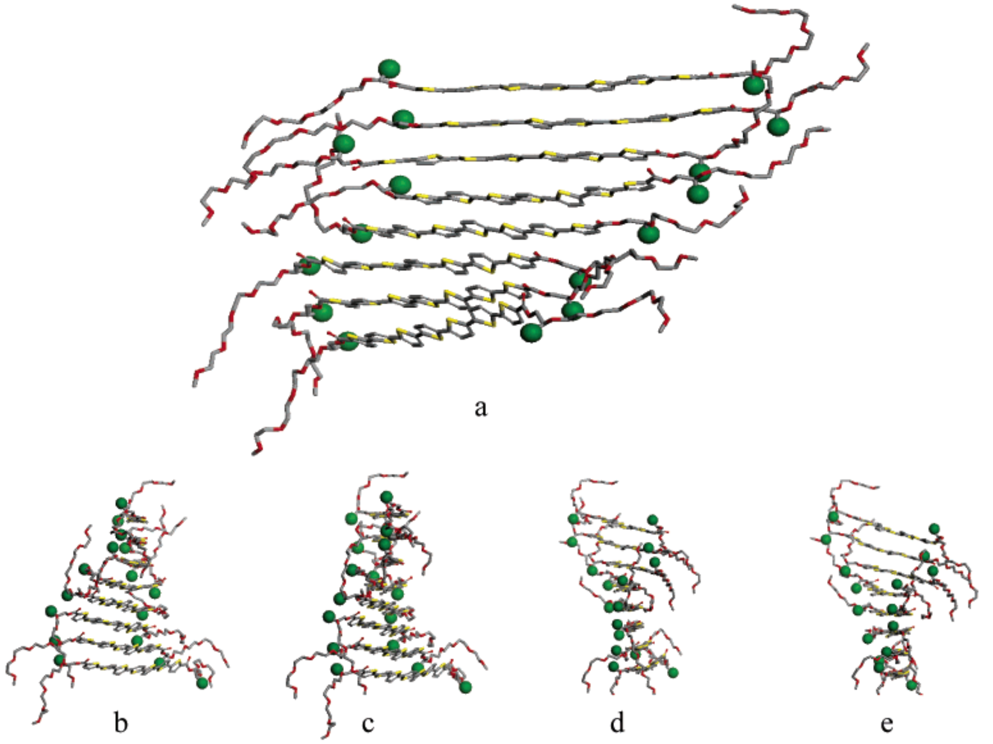

Figure 5. Side view of a column of **T7**β**S** molecules. The hydrogen atoms are omitted, for the sake of clarity. The carbon atoms of the methyl groups at the chiral centers are represented as green balls. In the top molecule, the T7 segment is oriented parallel (a) or perpendicular (b) to the page; views c, d, and e correspond to successive rotations by 15° along the vertical axis, starting from b.

correspond to a helical pitch of around 18 nm. Analogous results were obtained for the other enantiomer **T7**β**R.** However, in this case the left-handed helix is the most stable structure.

Two series of simulations were also carried out for two adjacent columns of **T6**β**R** molecules and **T5**β**S** molecules, respectively. In those cases, also distances between the cofacial

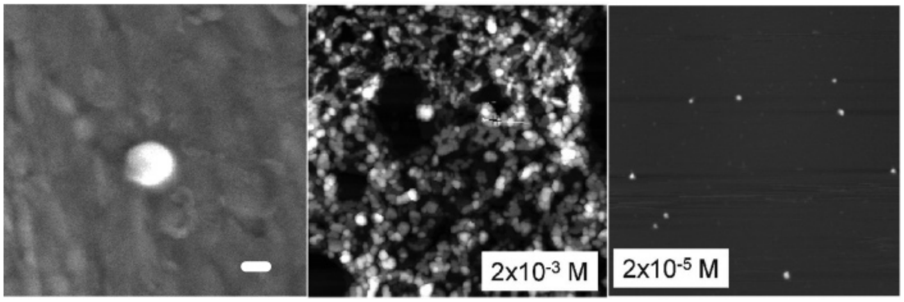

Figure 6. Images of drop cast solution of **T6βS** (butanol). (a) SEM image on an Al surface (scale bar represent 100 nm). TM-AFM images on glass, (b) height, 5 × 5 μm^2 scale 25 nm; (c) 1.8 × 1.8 μm^2 scale 15 nm.

molecules is found to be 3.7 ± 0.5 Å for both, while the angle measured between the main axis of neighbor molecules within a stack is 2 ± 1° and 4 ± 1° for **T6βR** and **T5βS**, respectively. For the **T5βS** molecular stack, the right-handed helix and, for the **T6βS** molecular stack, the left-handed helix were obtained. These data are in full agreement with the experimental data, providing additional evidence for the odd−even effect. Note should be made that in the modeling of the **T6βS** assemblies three interconverting structures were observed: a right-handed helix equilibrated via a straight column with a left-handed helix, with the latter having the highest stability. The smaller calculated energy difference between supramolecular assemblies formed by **T6** in comparison with **T5** and **T7** could be due to the difference in point group.[19,20] Even-numbered oligothiophenes possess a quasi-inversion center resulting in C_{2h} symmetry, while odd-numbered oligothiophenes have a C2 axis in the molecular plane and perpendicular to the long molecular axis (C_{2v}). This implies that for odd-numbered oligothiophenes the transition dipole moment is perfectly aligned with the long molecular axis, while for even oligomers there is an offset resulting in a different packing of odd- and even-numbered thiophenes. Finally, another interesting value that can be derived from the simulations is the average intermolecular interaction energy per molecule, $E_{\mathrm{T}n}$. The E_{T5}, E_{T6}, and E_{T7} energies are calculated to be 661, 741, and 795 kJ/mol, respectively,[21] showing that the molecular simulations are consistent with the increasing values of the melting temperature measured for the **T5**, **T6**, and **T7** aggregates.

Shape of Aggregates. The shape of the aggregates of **T6βS** in butanol solution was studied by dynamic light scattering (DLS). Spherical objects were revealed having an average radius of 55 nm at 293 K, which could be visualized by scanning electron microscopy (SEM, Figure 6a) and tapping mode atomic force microscopy (TM-AFM, Figure 6b,c). The shapes of the aggregates are similar as previously found in 2-propanol solution.[10] Clusters of the capsules were observed when a concentrated solution was applied to a glass surface (2 × 10^{-3} M, Figure 6b). The AFM images showed spherical objects 100 nm in diameter, based on the height using low tip forces. Isolated and much smaller spheres of 20 nm in diameter were observed after depositing a 2 × 10^{-5} M solution.

The assemblies are presumed to be constructed from a layer of **T6βS** molecules forming capsules, i.e., hollow spheres, similar to those found for oligo(*p*-phenylenevinylene)s and oligothiophene-based surfactants, which form vesicles in water.[10,22] It is difficult to construct vesicles from helically organized oligothiophenes. Therefore, we believe that self-assembled chiral domains are present in the shell of the macroscopic capsules.

Conclusions

We have comprehensively studied the chiroptical properties of a series of chiral self-assembled oligothiophenes. These studies show that the stability of the assemblies depends on the π-conjugation length and the position of the stereocenter relative to the π-conjugated core. Odd−even effects are observed in the sign of the Cotton effect as the position of the chiral substituent is moved along the oligo(ethylene oxide) chain. Moreover, the sign alternates on going from the quinquethiophene to the septithiophene having the same side chain. The stability of the assemblies is the largest for the achiral sexithiophenes, which reveals a competition between the packing of the π-conjugated segments and the chiral ethylene oxide side chains. It also shows that the perfect packing of oligo- and polythiophenes is found in which the angle between the long axis of adjacent thiophene segments is zero. Our results give some initial design rules for the construction of helical assemblies, which is important for any putative applications.

Acknowledgment. This research was carried out in the framework of the European Commission Training and Mobility of Researchers Networks LAMINATE (Contract Number HPRN-CT-2000-00135). We thank the EPSRC and Durham University for provision of facilities. This work was carried out in the framework of the EU-Integrated Project NAIMO (NMP4-CT-2004-500355). Research in Mons is partly supported by the InterUniversity Attraction Pole Program (PAI V/3) of the Belgian Federal Government, the European Commission, the Government of the Region of Wallonia (Phasing Out − Hainaut), and the Belgian National Fund for Scientific Research FNRS/FRFC. Ph.L. is Chercheur Qualifié of the “Fonds National de la Recherche Scientifique” (FNRS-Belgium). The research in Eindhoven was supported by the Council for Chemical Sciences of The Netherlands Organization for Scientific Research (CW-NWO).

Supporting Information Available: Experimental procedures for all compounds and techniques and theoretical methodology used. This material is free of charge via the Internet at http://pubs.asc.org.

JA0607234

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