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Chiral Aggregates of α,ω-Disubstituted Sexithiophenes in Protic and Aqueous Media

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Detailed conformational knowledge of folded polymers and oligomers as well as supramolecular assemblies in protic solvents, including water, is of great current interest.[1] An intriguing question relates to whether the assembly exists in a disordered collapsed state or as a unique structure with a well-defined conformation and if a disordered state is present between the well-defined folded structure or aggregate and the unfolded or disassembled state. For assemblies in protic solvents, like chromonics in water, detailed information concerning conformational uniqueness is scarce.[2] Recently, Moore et al. showed that in the folding process for a series of oligo(*m*-phenylene ethynylene)s, formation of a disordered state precedes that of a unique helical conformation.[3] Introduction of a side-chain stereocenter has proved to be an informative probe for studying the expression of chirality at the supramolecular level, leading to conformational information.[3,4] Most notably π-conjugated polymers and their mode of aggregation in apolar media have been studied, making use of the conformationally sensitive $\pi-\pi^*$ transition.[5,6] Here we report results concerning the synthesis of sexithiophene carrying chiral (2*S*)-2-methyl-3,6,9,12,15-pentaoxahexadecyl esters at both the α- and ω-positions and its supramolecular organization in protic solvents.

Interest in processable semiconducting oligo- and polythiophenes arises from their potential for use in electronic devices.[7] Generally, polythiophenes form less organized superstructures than oligomers because of defects in molecular structural homogeneity introduced during synthesis, and consequently several groups are involved in the synthesis and characterization of well-defined oligothiophenes.[8−13] Attempts to solubilize sexithiophene by substituting at the α- and ω-positions have been reported[13,14] but no information is available about the aggregation of oligothiophenes in protic solvents.

The α,ω-disubstituted sexithiophene used in this report, 2,2′:5′,2′′:5′′,2′′′:5′′′,2′′′′:5′′′′,2′′′′′-sexithiophene-5,5′′′′′-dicarboxylic acid (2*S*)-2-methyl-3,6,9,12,15-pentaoxahexadecyl ester **6**, was synthesized from 2,2′-bithiophene **1**,[15] which was deprotonated with 1 equiv of *n*-butyllithium at −78 °C and reacted with carbon dioxide (Scheme 1). Acidic workup gave 2,2′-bithiophene 5-carboxylic acid **2** which, on NBS bromination in DMF at 0 °C, gave **3**, 5′-bromo-2,2′-bithiophene-5-carboxylic acid. Refluxing **3** in thionyl chloride and recrystallization from hexane gave 5′-bromo-2,2′-bithiophene-5-carbonyl chloride **4** as yellow needles. (2*S*)-2-Methyl-3,6,9,12,15-pentaoxahexadecanol, derived from (L)-ethyl lactate using standard synthetic transformations,[16−18] reacted with the acid chloride **4** to give the ester **5** which was coupled with 5,5′-bis(trimethylstannyl)-2,2′-bithiophene[19] in the presence of a catalytic amount of tetrakis(triphenylphosphine)palladium(0) at 120 °C. Repeated column chromatography (BIORAD, BioBeads SX-1, dichloromethane) of the crude product gave pure diester **6** as a red solid.

Compound **6** shows high solubility in organic solvents (for example THF or *n*-butyl alcohol) and water. The UV/vis absorption spectrum in THF shows a structureless band at $\lambda_{\max} = 452$ nm as expected for molecularly dissolved sexithiophene chromophores (Figure 1).[13] The fluorescence spectrum has a maximum at 528 nm and shows the vibronic fine structure typical of molecular dissolution, while the high fluorescence intensity and the lack of a CD signal also support the absence of aggregation in this solvent.

The UV/vis absorption spectrum of **6** in *n*-butyl alcohol at 0 °C (Figure 2) is typical for aggregated sexithiophene derivatives with a blue shift of the main band of ca. $\Delta\lambda = 50$ nm to $\lambda_{\max} = 403$ nm. The fluorescence intensity is reduced, consequent on the dipole forbidden transition in the aggregate, and a bisignate CD effect is observed exhibiting a negative Cotton effect at lower ($\lambda = 458$ nm, 2.71 eV, $g_{\text{abs}} = \Delta\epsilon/\epsilon = -2.91 \times 10^{-2} \pm 0.2 \times 10^{-3}$) and a positive Cotton effect at higher energy ($\lambda = 376$ nm, 3.30 eV, $g_{\text{abs}} = (+9.9 \pm 0.2) \times 10^{-3}$). The zero-crossing close to the absorption maximum of the chromophore strongly indicates exciton coupling due to aggregated sexithiophene rods forming a chiral superstructure.[6] Circular polarization of the fluorescence of **6** in *n*-butyl alcohol could be observed with a maximum dissymmetry factor (g_{lum}) of $(-2.2 \pm 0.2) \times 10^{-3}$ at $\lambda = 650$ nm for which the sign is in agreement with the sign of the CD at lowest energy. Hence, a well-defined chiral aggregate is formed in *n*-butyl alcohol at 0 °C, that not only possesses a chiral ground state but also a chiral excited state as well, indicating that the chirality is the result of “cholesteric ordering”.

This aggregation was studied by temperature-dependent (−10 to 80 °C) CD and fluorescence spectroscopy. The solution was

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(20) In apolar solvents such as hexane the same type of absorption spectrum was found. Also, $\lambda_{\max}$ for **6** in water does not change in the concentration range 2.6×10^{-5} to 5.2×10^{-6} M indicating that if there is a critical aggregate concentration it is less than 10^{-6}.

(21) Determination of the aggregation number will be carried out in the future by the sergeant and soldiers method, see ref 4.

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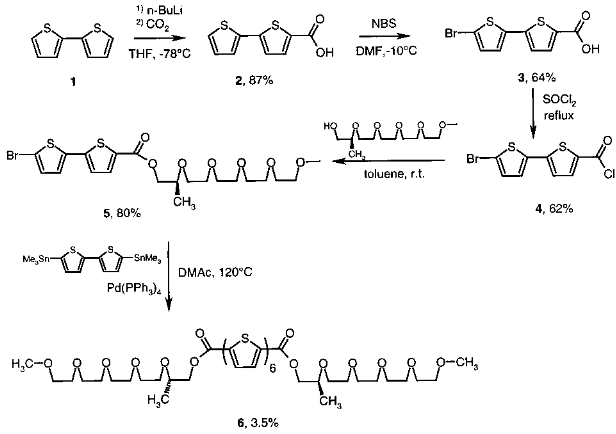
Scheme 1



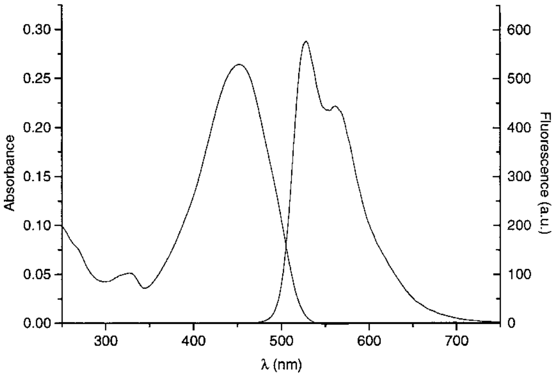


Figure 1. UV/vis and fluorescence spectrum ($\lambda_{\text{excitation}} = 400$ nm) of **6** in THF (3.9×10^{-6} mol l^{-1}) at room temperature.

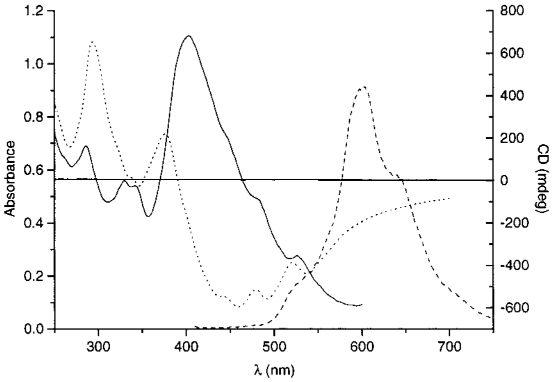


Figure 2. UV/vis (solid line), CD (dotted line), and PL ($\lambda_{\text{excitation}} = 400$ nm, dashed line) spectra of **6** in *n*-butyl alcohol (2.6×10^{-5} mol l^{-1}) at 0 °C. The PL spectrum is plotted in arbitrary units.

warmed stepwise from −10 to 80 °C with 10 min allowed for equilibration at each recording temperature. Plotting the CD intensity at $\lambda = 293$ nm against temperature shows a sharp CD signal disappearance at 30 °C (Figure 3). Fluorescence spectra of **6** in *n*-butyl alcohol were recorded at temperatures from −10 to 50 °C with $\lambda_{\text{ex}} = 400$ nm, where the fluorescence maximum is at 600 nm below 30 °C and at 533 nm above. The plot of fluorescence intensity ($\lambda = 533$ nm) against temperature shows an increase of luminescence with a transition at 30 °C, as for the CD plot (Figure 3). The phase transition is fully reversible as shown by data from cooling runs (not reproduced here). These results show unambiguously that chiral aggregates break up and form directly rather than via a disordered state.

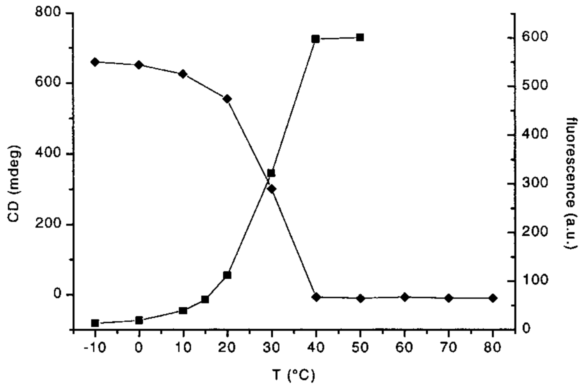


Figure 3. Intensity of the CD effect at $\lambda = 293$ nm (diamonds) and fluorescence intensity observed at $\lambda = 533$ nm ($\lambda_{\text{excitation}} = 400$ nm, squares) of **6** in *n*-butyl alcohol (2.6×10^{-5} mol l^{-1}) as a function of temperature.

Also compound **6** shows aggregation in water at room temperature. The UV/vis absorption spectrum is typical for aggregated sexithiophene derivatives with the main band at $\lambda_{\max} = 406$ nm.[20] The fluorescence is red shifted (600 nm) and reduced in intensity indicating aggregation and a bisignate CD effect is observed, exhibiting a negative Cotton effect at lower ($\lambda = 434$ nm, 2.86 eV, $g_{\text{abs}} = (-2.7 \pm 0.2) \times 10^{-3}$) and a positive Cotton effect at higher ($\lambda = 397$ nm, 3.12 eV, $g_{\text{abs}} = (+1.6 \pm 0.2) \times 10^{-3}$) energy with the CD signal going through zero near the absorption maximum of the chromophore. The shapes of the CD traces in water and *n*-butyl alcohol differ, which might be due to specific interactions between the side chains and the solvents, resulting in the formation of different aggregates. Circular polarization of the luminescence is observed with a maximum dissymmetry factor (g_{lum}) of $(-4.8 \pm 0.5) \times 10^{-3}$ which is in agreement with the sign of the CD at lowest energy.

To investigate whether a chiral superstructure was formed in the solid state, a drop cast film of **6** (from THF solution) was prepared and examined spectroscopically. Despite a relatively low absorption at the absorption maximum, an even more intense CD effect than the one measured in aqueous solution was observed. The CD signal passed through zero near the chromophore absorption maximum with a negative Cotton effect at lower (408 nm, 3.04 eV, $g_{\text{abs}} = -2.42 \times 10^{-2} \pm 0.2 \times 10^{-3}$) and a positive Cotton effect at higher energy (377 nm, 3.29 eV, $g_{\text{abs}} = +2.71 \times 10^{-2} \pm 0.2 \times 10^{-3}$).

In summary, the chiral sexithiophene derivative described aggregates in protic polar solvents.[21] Remarkably, this is analogous to the aggregation of poly(3-alkylthiophene)s in apolar solvents.[6] Chiral supramolecular organization is induced by chirality in the α,ω-substitutents of the sexithiophene, while the combination of CD and fluorescence spectroscopy showed that only one unique structure is formed in protic solvents.

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Supporting Information Available: Experimental details for the syntheses of **2**−**6**, ^{1}H NMR and ^{13}C NMR data for **2**−**6**, experimental description of the spectroscopic studies, and UV−vis, CD, and PL spectra of **6** in water at different concentrations (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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