A Chiroptical Study of Chiral Λ- and X- Type Oligothiophenes Toward Modelling the Interchain Interactions of Chiral Conjugated Polymers

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A variety of chiral Λ-type and X-type oligothiophenes (**MDC 1–10**) was synthesized and studied by means of UV–vis and CD spectroscopy in order to model the chiral interchain interactions of conjugated polymers with optically active side chains in both neutral and oxidized state. It was found that, within the class of chiral Λ-type oligothiophenes, the interchain chiral exciton coupling was only present when using an electronwithdrawing imine linkage between the oligothiophene and the chiral unit (**MDC 7–9**). Together with the observed decrease in *g*-value (dissymmetry factor for absorption) by extending the oligothiophene moiety, these linkage and elongation restrictions impose crucial drawbacks on chiral Λ-type oligothiophenes as study model in both neutral and oxidized state. Therefore, a new chiral X-type oligothiophene (**MDC 10**) was developed that combines chiral exciton coupling in neutral state with the additional ability of oxidation.

Introduction

Conjugated polymers substituted with enantiomerically pure chiral side chains, such as alkyl-,[1–4] alkoxy-,[5] aryl-substituted[6] polythiophenes (PTs), poly(phenylenevinylene)s[7] (PPVs) and poly(phenylene ethynylene)s[8–10] (PPEs) have attracted a lot of attention from academia and industry during the last few decades. They show a remarkably strong tendency to aggregate in a chiral superstructure of planarized polymer chains. Therefore, in order to thoroughly understand the origin of their solid-state photophysical properties, not only the intrinsic features of the individual polymer chains should be taken into account but also the interchain interactions are of great importance. After all, they directly affect nontrivial parameters like the fluorescence quantum yield and the charge carrier mobility, which in turn govern the efficiency of devices like LEDs and FETs, respectively.

Recently, molecular face-to-face stacking models of (achiral) conjugated oligothiophenes were synthesized to model the interchain interactions in linear conjugated systems.[11–14] In the neutral state, an interchain exciton coupling was observed. Conversely, in the oxidized state, it was shown that interchain radical cation π-dimers play a significant role in the optical and electrical properties. These well-defined oligomer models validate computational approaches. Moreover, they give deeper insight in the possible interchain processes and mechanisms within dopable linear conjugated polymers in general.

When chirality is implemented by grafting enantiomerically pure chiral side chains on the conjugated backbone (PT, PPV, PPE, . . .), this symmetry break induces the formation of non linear (chiral) aggregates.[15] Not only the above-mentioned couplings will appear in the solid state but also chiral interactions will manifest. To experimentally model both interchain interactions, a chiral Λ-type oligothiophene, comprising a terthiophene coupled to a chiral cyclohexane moiety via an imine linkage, has been prepared and

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thoroughly investigated by Meijer et al.[16] With this chiral model compound the origin of the observed bisignate Cotton effect in the CD spectrum of (neutral) chiral conjugated polymers was effectively explained as arising from a chiral superstructure of predominantly planar chains that are helically oriented with respect to one another.

However, this model shows some crucial drawbacks for a more fundamental investigation of the chiral interchain interactions. First, the electronwithdrawing imine linkage, used for the coupling of the oligothiophene moiety to the chiral unit, induces a significant asymmetry within the $\pi-\pi^*$ transition of the oligothiophene, which does not exist in the analogous chiral conjugated polymer. Second, the imine bond decreases the oligothiophene electron density and in turn considerably raises the oxidation potential of the conjugated system. As a consequence, chiral interchain interactions in the oxidized state have not been considered. Third, such an imine bonding is very sensitive to hydrolysis and imposes some synthetical and manipulative restrictions.

In this manuscript, a series of new chiral Λ-type oligothiophenes with a single, double and triple bond linkage was synthesized to reduce the critical electronwithdrawing nature of the linkage. An electronrich bithiophene moiety was used as oligothiophene to ensure a facile oxidation and was coupled to a variety of chiral binaphthalene linkers (Figure 1). Their chiroptical properties were investigated and compared to a new class of analogous chiral Λ-type oligothiophenes exhibiting a DπA structure (**MDC 6–9**) by means of UV–vis and CD spectroscopy. Finally, a new oxidizable chiral X-type oligothiophene (**MDC 10**) was developed, which cruciform-like structure was inspired by the chiral superstructure of conjugated polymers with optically active pendant side chains.[16] The chiroptical properties in neutral state, as well as a qualitative picture in oxidized state are given.

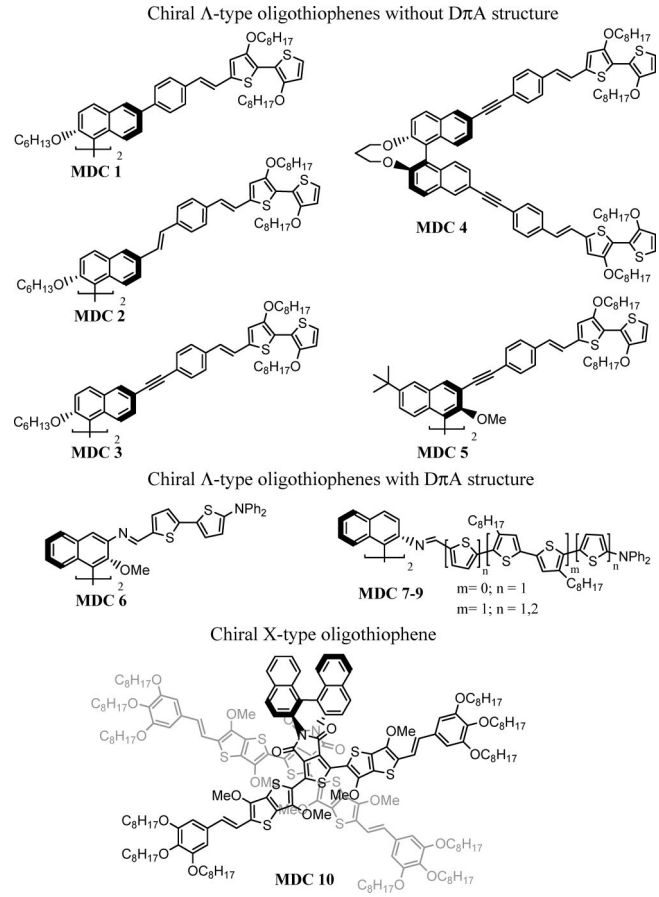

Figure 1. General overview of all the synthesized model compounds (**MDC 1–10**).

Experimental Section

Reagents and Instrumentations. All reagents were purchased from Aldrich Chemical Co., Acros Organics, Merck, Fluka, Alkemi and were used as received. Tetrahydrofuran (THF) and diethylether (Et_2O) were dried over a Na/K alloy. Dichloromethane was dried over molecular sieve (4Å). Dichloroethane, diisopropylamine, triethylamine (NEt_3), dimethylformamide (DMF), dioxane and toluene were freshly distilled and further dried on molecular sieve (4Å).

^{1}H and ^{13}C nuclear magnetic resonance (NMR) measurements were carried out with a Bruker Avance 300 MHz and a Bruker Avance 400 MHz. IR, UV–vis and CD spectra were recorded with a Perkin-Elmer 1600 series FTIR, a Varian Cary 400 and a JASCO 62 DS apparatus respectively. The gel permeation chromatography (GPC) measurements were carried out with a Shimadzu 10A apparatus with a tuneable absorbance detector and a differential refractometer in THF as eluent toward polystyrene standards. The DSC measurement was performed on a Perkin-Elmer DSC 7 apparatus.

1,[17] **5**,[18] **6**,[19] **8**,[20] **10**,[21] **11**,[22] **12**,[23] **13**,[24] **15**,[25] **18**,[26] **20**,[27] and **24**[28] were synthesized according to the literature procedures.

5-Formyl-3,3′-dioctyloxy-[2,2′-bithiophene] 2. A solution of **1** (2.20 mmol, 0.929 g) and DMF (3.30 mmol, 0.256 mL) in dry dichloroethane (7 mL) was purged with nitrogen and cooled to 0 °C. Slowly, phosphoryl chloride (2.42 mmol, 0.226 mL) was added and the reaction mixture was stirred for 1 h at 0 °C. The temperature was raised to 55 °C for 1 h. The mixture was poured into a NaOAc solution (20 mL, 1 M) and vigorously stirred for 1 h at room temperature. The mixture was extracted with dichloromethane and the combined organic layers were dried over $MgSO_4$. The solvents were removed and the product was isolated as yellow crystals.

Yield: 0.949 g (96%). Mp: 49.9–52.2 °C. ^{1}H NMR ($CDCl_3$; 300 MHz): δ 9.76 (s, 1H), 7.46 (s, 1H), 7.27 (d, $J = 5.5$ Hz, 1H), 6.88

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(d, $J = 5.5$ Hz, 1H), 4.16 (m, 4H), 1.89 (m, 4H), 1.55 (m, 4H), 1.45–1.20 (m, 16H), 0.89 (m, 6H). ^{13}C NMR ($CDCl_3$; 300 MHz): δ 182.4, 155.3, 152.4, 135.8, 126.7, 125.7, 122.3, 115.5, 112.6, 72.3, 31.9, 29.6, 29.5, 29.4, 29.3, 26.2, 26.1, 22.8, 14.3. MS: *m/z* 451 (M^+) (calcd 450.7), 339 ($M^+ - C_8H_{16}$), 226 ($M^+ - C_{16}H_{33}$), 197 ($M^+ - C_{16}H_{33}$, − CHO).

3,3′-Dioctyloxy-5-[2-(4-iodophenyl)ethenyl]-[2,2′-bithiophene] 3. A suspension of NaH (2.00 mmol, 48.0 mg) and **2** (1.96 mmol, 0.882 g) in THF (5 mL) was purged with argon and heated to 60 °C. A solution of **5** (2.00 mmol, 0.701 g) in THF (2 mL) was added under an argon atmosphere and the mixture was stirred for 30 min at 60 °C. The reaction mixture was poured into a HCl solution (10 mL, 1 M) and extracted with dichloromethane. The combined organic layers were dried over $MgSO_4$ and the solvents were removed. The crude compound was purified by column chromatography (silicagel, eluent: hexane:ethylacetate (80:20 v/v)) and isolated as a yellow solid.

Yield: 3.90 g (73%). Mp: 75.6–76.2 °C. ^{1}H NMR ($CDCl_3$; 400 MHz): δ 7.64 (d, $J = 8.4$ Hz, 2H), 7.17 (d, $J = 8.4$ Hz, 2H), 7.11 (d, $J = 16.2$ Hz, 1H), 7.10 (d, $J = 5.6$ Hz, 1H), 6.85 (s, 1H), 6.82 (d, $J = 5.6$ Hz, 1H), 6.78 (d, $J = 16.2$ Hz, 1H), 4.13 (t, 2H), 4.08 (t, 2H), 1.86 (m, 4H), 1.54 (m, 4H), 1.45–1.25 (m, 16H), 0.92–0.84 (m, 6H). ^{13}C NMR ($CDCl_3$; 300 MHz): δ 152.5, 152.0, 137.8, 136.9, 136.8, 127.9, 125.2, 123.1, 122.5, 116.1, 115.2, 114.5, 114.1, 92.4, 72.2, 72.0, 32.0, 29.9, 29.5, 29.4, 26.2, 22.8, 14.3. MS: *m/z* 650.9 (M^+) (calcd 650.8).

Diethyl-4-[2-(4-octyloxy-5-(3-octyloxy-(2-thienyl))-2-thienyl)ethenyl]benzylphosphonate 4. A suspension of NaH (6.00 mmol, 144 mg) and **6** (6.00 mmol, 2.27 g) in THF (5 mL) was purged with argon and heated to 60 °C. A solution of **2** (3.00 mmol, 1.35 g) in THF (5 mL) was added under an argon atmosphere and the mixture was stirred for 1 h at 60 °C. The reaction mixture was poured into a HCl solution (15 mL, 1 M) and extracted with dichloromethane. The combined organic layers were dried over $MgSO_4$ and the solvents were removed. The crude compound was purified by column chromatography (silicagel, eluent: ethylacetate:hexane (80:20 v/v)) and isolated as a yellow solid.

Yield: 0.719 g (36%). Mp: 80.7–82.3 °C. ^{1}H NMR ($CDCl_3$; 300 MHz): δ 7.40 (d, $J = 7.3$ Hz, 2H), 7.27 (d, $J = 7.3$ Hz, 2H), 7.11 (d, $J = 15.0$ Hz, 1H), 7.09 (d, $J = 5.5$ Hz, 1H), 6.86 (d, $J = 15.0$ Hz, 1H), 6.85 (s, 1H), 6.84 (d, $J = 5.5$ Hz, 1H), 4.12 (q, 4H), 4.02 (m, 4H), 3.15 (d, $J = 21.9$ Hz, 2H), 1.87 (m, 4H), 1.56 (m, 4H), 1.46–1.20 (m, 22H), 0.88 (m, 6H). ^{13}C NMR ($CDCl_3$; 300 MHz): δ 152.4, 151.9, 137.4, 135.9, 130.8, 130.7, 130.2, 126.4, 126.1, 122.2, 116.2, 114.8, 114.3, 114.0, 72.2, 72.0, 62.3, 32.0, 31.9, 29.9, 29.8, 29.4, 29.3, 26.3, 26.2, 22.8, 16.6, 16.5, 14.3. MS: *m/z* 675 (M^+) (calcd 675.0), 451 ($M^+ - C_{16}H_{32}$).

(*S*)-6,6′-Bis(pinacolato)diboron-2,2′-dihexyloxy-[1,1′-binaphthalene] 7. A solution of **12** (3.00 mmol, 1.84 g) in dry THF (10 mL) was purged with argon and cooled at −78 °C. Under an argon atmosphere, *n*-BuLi (6.30 mmol, 2.52 mL, 2.5 M in hexane) was added and the mixture was stirred for 15 min at −78 °C. The reaction mixture was added to trimethylborate (16.0 mmol, 1.83 mL) under an argon atmosphere and was slowly allowed to reach room temperature for 4 h. It was poured into a HCl solution (10 mL, 1 M) and extracted with ethylacetate. The combined organic layers were washed with a saturated NaCl solution and dried over $MgSO_4$. The solvents were removed and the crude compound was purified by column chromatography (silicagel, eluent:hexane: ethylacetate (20:80 v/v)). The product was redissolved in dry toluene (8 mL) and $MgSO_4$ (10.0 mmol, 1.20 g) and pinacol (20.0 mmol, 2.36 g) were added. The mixture was stirred for 15 min at room temperature. The product was extracted with dichloromethane and isolated as white crystals.

Yield: 0.656 g (31%). Mp: 46.8–52.6 °C. ^{1}H NMR ($CDCl_3$; 300 MHz): δ 8.38 (s, 2H), 7.97 (d, $J = 8.2$ Hz, 2H), 7.54 (d, $J = 8.2$ Hz, 2H), 7.38 (d, $J = 8.2$ Hz, 2H), 7.11 (d, $J = 8.2$ Hz, 2H), 3.92 (m, 4H), 1.50–1.30 (m, 28H), 1.10–0.80 (m, 12H), 0.72 (t, 6H). ^{13}C NMR ($CDCl_3$; 300 MHz): δ 155.6, 136.5, 136.0, 130.7, 130.1, 128.6, 124.6, 120.3, 115.5, 83.7, 69.5, 31.4, 29.4, 25.4, 25.0, 22.6, 14.1. MS: *m/z* 707 (M^+) (calcd 706.7), 581 ($M^+ - C_6H_{11}BO_2$), 285 ($M^+ - C_{12}H_{22}B_2O_4$, $- C_{12}H_{26}$).

(*S*)-6,6′-Diethynyl-2,2′-(1,3-propylenedioxy)-[1,1′-binaphthalene] 9. A solution of **13** (1.00 mmol, 0.334 g) in DMF (4 mL) was slowly added to a suspension of NaH (2.00 mmol, 48.0 mg) in DMF (1 mL) at room temperature. The reaction mixture was heated to 80 °C and a solution of 1,3-dibromopropane (1.10 mmol, 0.222 g) and NaI (0.200 mmol, 30.0 mg) in DMF (4 mL) was added. The reaction was completed after 12 h stirring at 80 °C. The mixture was poured into water (20 mL) and extracted with a hexane−diethylether mixture (1/1). The combined organic layers were washed with a saturated $NaHCO_3$ solution, a HCl solution (1 M) and a saturated NaCl solution and further dried over $MgSO_4$. The solvents were removed and the crude compound was purified by column chromatography (silicagel, eluent: hexane:dichloromethane (70:30 v/v)) and isolated as white crystals.

Yield: 0.147 g (46%). Mp: 176.3–180.8 °C. ^{1}H NMR ($CDCl_3$; 300 MHz): δ 8.07 (s, 2H), 7.92 (d, $J = 9.1$ Hz, 2H), 7.47 (d, $J = 9.1$ Hz, 2H), 7.29 (d, $J = 9.1$ Hz, 2H), 7.16 (d, $J = 9.1$ Hz, 2H), 4.36 (m, 4H), 3.11 (s, 2H), 1.97 (m, 2H). ^{13}C NMR ($CDCl_3$; 300 MHz): δ 155.9, 133.1, 132.8, 130.0, 129.9, 129.3, 126.2, 123.7, 120.1, 117.9, 84.1, 77.3, 72.1, 30.7. MS: *m/z* 375 (M^+) (calcd 374.4), 334 ($M^+ - C_3H_5$).

MDC 1. A solution of **7** (0.215 mmol, 0.152 g), **3** (0.538 mmol, 0.350 g) and $Pd[PPh_3]_4$ (0.0215 mmol, 24.8 mg) in THF (5 mL) was purged with argon and heated to 60 °C. Under an argon atmosphere, a solution of K_2CO_3 (25.0 mmol, 3.46 g) in water (25 mL) was slowly added. The reaction was completed after 24 h stirring at 60 °C, poured into a HCl solution (1 M) and extracted with dichloromethane. The combined organic layers were washed with a saturated NaCl solution and dried over $MgSO_4$. The solvents were removed and the crude compound was purified by column chromatography (silicagel, eluent:hexane:ethylacetate (90:10 v/v)) and isolated as a red solid.

Yield: 0.968 g (30%). Mp: 48.8–54.0 °C. ^{1}H NMR ($CDCl_3$; 400 MHz): δ 8.09 (s, 2H), 7.99 (d, $J = 8.9$ Hz, 2H), 7.67 (d, $J = 8.2$ Hz, 4H), 7.53 (d, $J = 8.2$ Hz, 4H), 7.51 (d, $J = 8.1$ Hz, 2H), 7.44 (d, $J = 8.9$ Hz, 2H), 7.26 (d, $J = 8.1$ Hz, 2H), 7.16 (d, $J = 16.0$ Hz, 2H), 7.09 (d, $J = 5.6$ Hz, 2H), 6.93 (d, $J = 16.0$ Hz, 2H), 6.87 (s, 2H), 6.84 (d, $J = 5.6$ Hz, 2H), 4.13 (t, 4H), 4.11 (t, 4H), 3.97 (m, 4H), 1.88 (m, 8H), 1.54 (m, 12H), 1.45–1.20 (m, 32H), 1.10–0.92 (m, 12H), 0.91–0.82 (m, 12H), 0.72 (t, 6H). ^{13}C NMR ($CDCl_3$; 300 MHz): δ 154.9, 152.4, 152.0, 140.2, 137.6, 136.0, 135.6, 133.6, 129.6, 127.5, 127.2, 126.9, 126.6, 126.1, 125.6, 125.5, 121.8, 120.5, 116.1, 114.4, 114.0, 72.2, 72.0, 69.8, 32.0, 31.9, 31.5, 29.9, 29.8, 29.5, 29.4, 26.3, 26.2, 25.5, 22.8, 22.6, 14.6, 14.3, 13.9. MS: *m/z* = 1500.8 (M^+) (calcd 1500.2).

MDC 2. A suspension of NaH (0.484 mmol, 11.6 mg) and **11** (0.193 mmol, 98.8 mg) in THF (1 mL) was purged with argon and heated to 60 °C. A solution of **4** (0.484 mmol, 0.327 g) in THF (2 mL) was added under an argon atmosphere and the mixture was stirred for 2 h at 60 °C. The reaction mixture was poured into a HCl solution (10 mL, 1 M) and extracted with dichloromethane. The combined organic layers were washed with a saturated NaCl solution and dried over $MgSO_4$. The solvents were removed and the crude compound was triturated with a mixture of ethylacetate: hexane (80:20 v/v) and isolated as a red solid.

Yield: 0.114 g (38%). Mp: 129.8–133.3 °C. ^{1}H NMR ($CDCl_3$; 400 MHz): δ 7.92 (d, J = 8.9 Hz, 2H), 7.87 (s, 2H), 7.49 (d, J = 8.5 Hz, 4H), 7.47 (d, J = 8.7 Hz, 2H), 7.43 (d, J = 8.5 Hz, 4H), 7.40 (d, J = 8.9 Hz, 2H), 7.25 (d, J = 16.0 Hz, 2H), 7.16 (d, J = 8.7 Hz, 2H), 7.13 (d, J = 16.0 Hz, 2H), 7.10 (d, J = 16.0 Hz, 2H), 7.08 (d, J = 5.6 Hz, 2H), 6.88 (d, J = 16.0 Hz, 2H), 6.85 (s, 2H), 6.83 (d, J = 5.6 Hz, 2H), 4.13 (t, 4H), 4.11 (t, 4H), 3.94 (m, 4H), 1.87 (m, 8H), 1.56 (m, 12H), 1.45–1.25 (m, 32H), 1.10–0.92 (m, 12H), 0.91–0.83 (m, 12H), 0.73 (t, 6H). ^{13}C NMR ($CDCl_3$; 300 MHz): δ 155.0, 152.4, 152.0, 137.6, 136.9, 136.4, 134.0, 132.7, 129.5, 126.8, 126.4, 120.8, 114.4, 114.1, 72.2, 72.1, 69.8, 32.0, 29.5, 26.3, 26.2, 22.8, 22.6, 14.2, 14.0. MS: m/z 1552.7 (M^+) (calcd 1552.3).

MDC 3. A solution of **3** (0.384 mmol, 0.500 g) and $Pd[PPh_3]_4$ (9.60 μmol, 11.8 mg) in dry THF (0.5 mL) and diisopropylamine (0.5 mL) was purged with argon. Succesively, a solution of **8** (0.192 mmol, 96.5 mg) in THF (0.5 mL) and a solution of CuI (0.0384 mmol, 7.31 mg) in diisopropylamine (0.5 mL) were added under an argon atmosphere. The mixture was stirred at 60 °C for 4.5 h, poured into a HCl solution (5 mL, 1 M) and extracted with dichloromethane. The combined organic layers were washed with a HCl solution (1 M), a saturated $NaHCO_3$ solution and a saturated NaCl solution and dried over $MgSO_4$. The solvents were removed and the crude compound was purified by column chromatography (silicagel, eluent: hexane:ethylacetate: (80:20 v/v)) and isolated as a red solid.

Yield: 34.2 mg (11%). Mp: 85.4–89.3 °C. ^{1}H NMR ($CDCl_3$; 400 MHz): δ 8.06 (d, J = 1.5 Hz, 2H), 7.90 (d, J = 8.9 Hz, 2H), 7.50 (d, J = 8.4 Hz, 4H), 7.42 (d, J = 8.4 Hz, 4H), 7.41 (d, J = 8.9 Hz, 2H), 7.31 (dd, J = 8.8 Hz, J = 1.5 Hz, 2H), 7.14 (d, J = 16.0 Hz, 2H), 7.12 (d, J = 8.8 Hz, 2H), 7.09 (d, J = 5.6 Hz, 2H), 6.87 (d, J = 16.0 Hz, 2H), 6.86 (s, 2H), 6.83 (d, J = 5.6 Hz, 2H), 4.13 (t, 4H), 4.10 (t, 4H), 3.94 (m, 4H), 1.87 (m, 8H), 1.56 (m, 12H), 1.45–1.20 (m, 32H), 1.10–0.90 (m, 12H), 0.90–0.80 (m, 12H), 0.76 (t, 6H). ^{13}C NMR ($CDCl_3$; 300 MHz): δ = 155.4, 152.5, 152.0, 151.0, 137.2, 137.0, 133.7, 132.0, 131.6, 129.3, 128.8, 128.6, 126.2, 125.9, 123.0, 122.5, 122.3, 120.0, 118.1, 116.1, 114.5, 114.2, 97.5, 89.5, 72.2, 72.1, 69.6, 32.0, 31.9, 31.4, 29.9, 29.8, 29.6, 29.5, 29.4, 29.3, 26.3, 26.2, 25.5, 22.8, 22.6, 14.3, 14.1. MS: m/z 1548.9 (M^+) (calcd 1548.3).

MDC 4. The procedure described for the preparation of **MDC 3** was followed, starting from **9** (0.200 mmol, 0.749 g). The crude compound was triturated with a mixture of hexane:ethylacetate (60:40 v/v) and isolated as a red solid.

Yield: 0.150 g (53%). Mp: 154.3–159–9 °C. ^{1}H NMR ($CDCl_3$; 400 MHz): δ 8.10 (s, 2H), 7.94 (d, J = 9.1 Hz, 2H), 7.51 (d, J = 8.2 Hz, 4H), 7.48 (d, J = 9.1 Hz, 2H), 7.43 (d, J = 8.2 Hz, 4H), 7.36 (d, J = 9.1 Hz, 2H), 7.22 (d, J = 9.1 Hz, 2H), 7.15 (d, J = 16.0, 2H), 7.10 (d, J = 5.4 Hz, 2H), 6.88 (d, J = 16.0 Hz, 2H), 6.87 (s, 2H), 6.84 (d, J = 5.4 Hz, 2H), 4.39 (m, 4H), 4.13 (t, 4H), 4.11 (t, 4H), 1.99 (m, 2H), 1.87 (m, 8H), 1.54 (m, 8H), 1.45–1.15 (m, 32H), 0.90–0.75 (m, 12H). ^{13}C NMR ($CDCl_3$; 300 MHz): δ 155.7, 152.5, 152.0, 137.1, 132.8, 132.2, 131.8, 130.1, 126.3, 126.0, 123.7, 122.0, 119.2, 114.5, 91.0, 90.0, 72.2, 72.0, 32.0, 29.9, 29.8, 29.5, 29.4, 29.3, 26.3, 26.2, 22.8, 14.6, 14.3, 13.9. MS: m/z 1419.8 (M^+) (calcd 1420.4).

MDC 5. The procedure described for the preparation of **MDC 3** was followed, starting from **10** (0.200 mmol, 0.949 g). The crude compound was washed with hot hexane and isolated as a red solid.

Yield: 0.107 g (35%). Mp: 80.1–88.4 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.44 (d, J = 2.0 Hz, 2H), 7.68 (s, 2H), 7.65 (d, J = 8.4 Hz, 4H), 7.51 (d, J = 8.4 Hz, 4H), 7.36 (dd, J = 9.1 Hz, J = 2.0 Hz, 2H), 7.19 (d, J = 15.8 Hz, 2H), 7.12 (d, J = 9.1 Hz, 2H), 7.11 (d, J = 5.6 Hz, 2H), 6.91 (d, J = 15.8 Hz, 2H), 6.89 (s, 2H), 6.85 (d, J = 5.6 Hz, 2H), 4.15 (t, 4H), 4.12 (t, 4H), 3.78 (s, 6H), 1.89 (m, 8H), 1.56 (m, 8H), 1.43 (s, 18H), 1.40–1.25 (m, 32H), 0.93–0.84 (m, 12H). ^{13}C NMR (300 MHz, $CDCl_3$): δ = 154.0, 152.6, 152.0, 147.2, 137.4, 137.1, 132.2, 131.9, 129.2, 126.9, 126.2, 125.8, 122.1, 122.0, 121.3, 120.9, 117.9, 114.6, 114.2, 95.2, 89.2, 72.2, 72.1, 35.0, 32.0, 31.4, 31.2, 30.9, 22.8. MS: m/z 1519.8 (M^+) (calcd 1520.2).

(*R*)-3,3′-Diamino-2,2′-dimethoxy-[1,1′-binaphthalene] 16. A solution of **15** (1.34 mmol, 540 mg) and NEt_3 (6.2 mmol, 880 μL) in THF (10 mL) was purged with argon. Diphenylphosphonic azide (2.95 mmol, 560 μL) was added dropwise. The reaction was allowed to proceed at room temperature for 4 h. H_2O (3 mL) was added and the reaction mixture was brought to reflux for 4 h. The reaction mixture was poured into aqueous solution of K_2CO_3 (10 mL, 2M) and extracted with dichloromethane. The combined organic layers were washed with water and dried over $MgSO_4$. The solvents were removed and the crude compound was purified by column chromatography (silicagel, eluent: petroleum ether:ethyl acetate (60:40 v/v)).

Yield: 117 mg (26%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (d, J = 8.2 Hz, 2H), 7.19 (ddd, J = 7.2 Hz, J = 7.2 Hz, J = 1.8 Hz, 2H), 7.20 (s, 2H), 7.03 (m, 4H), 3.33 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 147.3, 139.9, 132.2, 128.6, 126.3, 125.1, 125.0, 123.1, 110.2, 60.3.

MDC 6. A solution of **16** (0.150 mmol, 51.7 mg) and **17** (0.300 mmol, 108 mg) in dry dichloromethane (1.5 mL) was charged with activated molecular sieve (4Å). The reaction was allowed to proceed at room temperature for 48 h. The solvent was removed and the crude compound was purified by successively trituration in methanol and isolated as a red solid.

Yield: 71.0 mg (45.9%). Mp: 148.7–150.2 °C. ^{1}H NMR (400 MHz, CD_2Cl_2): δ = 8.65 (s, 2H), 7.80 (d, J = 8.0 Hz, 2H), 7.54 (s, 2H), 7.37 (d, J = 3.4 Hz, 2H), 7.30 (t, J = 8.0 Hz, 2H), 7.21 (t, J = 8.0 Hz, 8H), 7.11 (t, J = 8.0 Hz, 2H), 7.10 (d, J = 8.0 Hz, 8H), 7.05 (d, J = 3.4 Hz, 2H), 7.03 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 3.4 Hz, 2H), 7.00 (t, J = 4.0 Hz, 4H), 6.48 (d, J = 3.4, 2H), 3.57 (s, 6H). ^{13}C NMR (75 MHz, CD_2Cl_2): δ = 153.9, 153.4, 151.2, 148.1, 143.8, 141.4, 138.1, 134.2, 133.0, 131.7, 129.9, 128.3, 126.3, 126.1, 125.7, 124.8, 124.4, 124.2, 123.8, 123.0, 120.6, 119.6, 117.8, 61.4. MS: m/z 1031.4 (M^+) (calcd 1031.3).

2-Formyl-3,6-dimethoxythieno[3,2-b]thiophene 19. A solution of **18** (5.00 mmol, 1.00 g) and DMF (7.50 mmol, 0.581 mL) in dry dichloroethane (10 mL) was purged with nitrogen and cooled to 0 °C. Slowly, phosphoryl chloride (5.50 mmol, 0.513 mL) was added and the reaction mixture was successively stirred for 1 h at 0 °C and for 1 h at 55 °C. The mixture was poured into a NaOAc solution (20 mL, 1 M) and vigorously stirred for 1 h at room temperature. After the hydrolysis, the reaction mixture was extracted with dichloromethane and the combined organic layers were washed with a HCl solution (1 M) and dried over $MgSO_4$. The solvents were removed and the product was isolated as a yellow solid.

Yield: 1.12 g (98%). Mp: 132.2 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.0 (s, 1H), 6.54 (s, 1H), 4.28 (s, 3H), 3.93 (s, 3H). ^{13}C NMR (300 MHz, $CDCl_3$): δ = 182.0, 158.2, 151.3, 136.1, 125.4, 122.9, 103.8, 59.8, 58.0. MS: m/z 229 (M^+) (calcd 228.3), 201 (M^+ −CHO).

Diethyl-3,4,5-trioctyloxybenzylphosphonate 21. A suspension of 3,4,5-trioctyloxybenzyl alcohol (5,00 mmol, 2.47 g) and triphenylphosphine (7.50 mmol, 1.97 g) in dry dichloromethane (5 mL) was cooled to 0 °C and shed from light. Small portions of *N*-bromosuccinimide (7.50 mmol, 1.33 g) were added and the mixture was stirred for 20 min at 0 °C. The reaction mixture was poured into water (10 mL) and extracted with dichloromethane. The combined organic layers were dried over $MgSO_4$ and the

solvent was removed. The crude, brown oil was dissolved in triethyl phosphite and the mixture was refluxed for 2 h. The volatile compounds were removed under reduced pressure. The crude compound was purified by column chromatography (silicagel, eluent:hexane:ethylacetate (60:40 v/v)) and isolated as a faintly yellow oil.

Yield: 2.18 (71%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ 6.47 (d, J = 1.8 Hz, 2H), 4.05–3.85 (m, 10H), 3.01 (d, J = 21 Hz, 2H), 1.85–1.63 (m, 6H), 1.54–1.40 (m, 6H), 1.39–1.26 (m, 24H), 1.24 (t, 6H), 0.88 (t, 9H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 153.0, 137.1, 126.3, 108.3, 73.4, 69.1, 62.2, 34.8, 33.0, 31.9, 30.3, 29.6, 29.4, 26.1, 22.7, 16.4, 14.1. MS: m/z 613 (M^+) (calcd 613.0), 501 ($M^+ - C_8H_{16}$), 389 ($M^+ - C_{16}H_{32}$).

3,6-Dimethoxy-2-[2-(3,4,5-trioctyloxyphenyl)ethenyl]thieno[3,2-b]thiophene 22. A suspension of NaH (2.50 mmol, 60.0 mg) and **19** (2.00 mmol, 0.457 g) in THF (3 mL) was purged with argon and heated to 60 °C. A solution of **21** (2.50 mmol, 1.56 g) in THF (1 mL) was added under an argon atmosphere. The reaction was completed after 2 h stirring at 60 °C. The mixture was poured into a HCl solution (10 mL, 1 M) and extracted with dichloromethane. The combined organic layers were dried over $MgSO_4$ and the solvents were removed. The crude compound was purified by column chromatography (silicagel, eluent: hexane:ethylacetate (80:20 v/v)) and isolated as an orange solid.

Yield: 1.01 g (74%). Mp: 34.4 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 7.21 (d, J = 16.4 Hz, 1H), 6.67 (d, J = 16.4, 1H), 6.67 (s, 2H), 6.30 (s, 1H), 4.10 (s, 3H), 3.99 (t, 4H), 3.92 (t, 2H), 3.91 (s, 3H), 1.81 (qu, 4H), 1.71 (qu, 2H), 1.57–1.43 (m, 6H), 1.40–1.20 (m, 24H), 0.89 (m, 9H). ^{13}C NMR (300 MHz, CD_2Cl_2): δ = 153.6, 151.4, 147.9, 138.1, 132.7, 128.4, 126.7, 126.3, 124.3, 118.2, 104.7, 98.3, 73.7, 69.3, 59.9, 57.9, 32.2, 32.1, 30.6, 29.9, 29.8, 29.7, 29.6, 27.2, 26.4, 23.0, 14.2. MS: m/z 687 (M^+) (calcd 687.1), 575 ($M^+ - C_8H_{16}$).

3,6-Dimethoxy-7-trimethyltin-2-[2-(3,4,5-trioctyloxyphenyl)ethenyl]thieno[3,2-b]thiophene 23. A solution of **22** (0.310 mmol, 0.216 g) in dry Et_2O (5 mL) was purged with argon and cooled at 0 °C. Under an argon atmosphere, *t*-BuLi (0.340 mmol, 0.230 mL, 1.5 M in pentane) was added and the mixture was vigorously stirred for 10 min at 0 °C. A solution of trimethyltin chloride (0.38 mmol, 75.0 mg) in dry Et_2O (1 mL) was added and the reaction mixture was stirred at room temperature for 1 h. The solvent was removed and the product was redissolved in hexane. LiCl was filtrated and, after removal of the solvent, the product was isolated as a brown oil.

Yield: 0.216 g (82%). ^{1}H NMR (300 MHz, CD_2Cl_2): δ = 7.20 (d, J = 16.4 Hz, 1H), 6.67 (s, 2H), 6.66 (d, J = 16.4 Hz, 1H), 4.12 (s, 3H), 4.00 (t, 4H), 3.96 (s, 3H), 3.93 (t, 2H), 1.82 (qu, 4H), 1.72 (qu, 2H), 1.56–1.43 (m, 6H), 1.40–1.20 (m, 24H), 0.89 (m, 9H), 0.40 (s, 9H). ^{13}C NMR (300 MHz, CD_2Cl_2): δ = 156.3, 153.6, 147.6, 138.1, 135.4, 132.8, 127.0, 126.3, 124.2, 120.1, 118.5, 104.7, 73.7, 69.3, 60.0, 59.9, 32.3, 32.2, 30.7, 29.9, 29.8, 29.7, 29.6, 26.5, 23.1, 14.3, −8.1. MS: m/z 687 ($M^+ - C_3H_8Sn$) (calcd M^+, 849.9), 575 ($M^+ - C_3H_8Sn$, $- C_8H_{16}$).

2,5-Dibromothiophene-3,4-carboxylic anhydride 25. A solution of **24** (1.06 mmol, 0.350 g) in acetic anhydride (156 mmol, 15.0 mL) was stirred for 2 h at 75 °C. The excess of acetic anhydride was removed under reduced pressure and the product was isolated as white crystals.

Yield: 0.264 g (80%). IR (NaCl): ν 1838, 1765 cm^{-1}. Mp: 189.4 °C. ^{13}C NMR (300 MHz, CD_2Cl_2): δ 154.4, 134.0, 117.5. MS: m/z = 313 (M^+) (calcd 311.9), 235 ($M^+ - Br$).

(*R*)-Bis-2,2′-[4,6-dibromo-1,3-dioxo-thieno-[3,4-c]-pyrol-2-yl]-[1,1′-binaphthalene] 27. A solution of **26** (0.310 mmol, 88.2 mg), **25** (0.700 mmol, 217 mg) and DMAP (0.840 mmol, 103 mg) in dry dioxane (4 mL) was stirred for 20 h at 55 °C. Acetic anhydride (26.4 mmol, 2.50 mL) was added and the mixture was heated to 80 °C. The reaction was completed after 4 h vigorously stirring at 80 °C. The mixture was poured into water (10 mL) and extracted with dichloromethane. The combined organic layers were dried over $MgSO_4$ and the solvents were removed. The crude compound was purified by column chromatography (silicagel, eluent:ethylacetate: dichloromethane (70:30 v/v)) and isolated as a yellow-brownish solid.

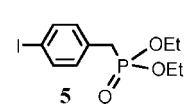
Yield: 182 mg (67%). IR (NaCl): ν 1764, 1724 cm^{-1}. Mp: 255–260 °C. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 8.02 (d, J = 9.2 Hz, 2H), 7.96 (d, J = 7.3 Hz, 2H), 7.57 (t, J = 7.3 Hz, 2H), 7.33 (t, J = 7.3 Hz, 2H), 7.29 (d, J = 9.2 Hz, 2H), 7.27 (d, J = 7.3 Hz, 2H). ^{13}C NMR (300 MHz, CD_2Cl_2): δ = 160.9, 158.0, 135.4, 134.4, 134.2, 133.6, 133.0, 130.4, 129.2, 128.9, 128.1, 127.3, 126.5, 125.9, 113.7. MS: m/z 873 (M^+) (calcd 872.2).

MDC 10. A solution of **27** (35,0 μmol, 30.5 mg), **23** (0.243 mmol, 206 mg), $Pd_2(dba)_3$ (4.38 μmol, 4.00 mg) and triphenylarsine (35.0 μmol, 10.7 mg) in THF (3 mL) was purged with argon and refluxed for 20 h. The reaction mixture was poured into cold methanol (15 mL) and the precipitate was filtered off. The crude compound was washed with acetone and isolated as a red solid.

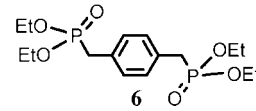
Yield: 50.0 mg (44%). IR (NaCl): ν 2917.8, 2850.5, 1747.3, 1704.0 cm^{-1}. MS (MALDI-TOF): m/z 3297.0 (calcd.: 3297.1).

Results and Discussion

Synthesis. *Chiral Λ-Type Oligothiophenes.* The synthesis of the chiral Λ-type oligothiophenes without a DπA structure (**MDC 1–5**) is presented in Scheme 1. The convergent synthetic pathway was developed based on the exploitation of the key bithiophene **2**, obtained by formylation of **1** using a Vilsmeier–Haack reaction. The choice of **1** relies on two different considerations. First, the two electronrich C_8 alkoxy chains increase the solubility and lower the oxidation potential. Second, the "head to head" substitution ensures a planarisation of the bithiophene unit due to attractive S−O interactions,[29,30] resulting in an efficient conjugation, which additionally lowers the oxidation potential.



5

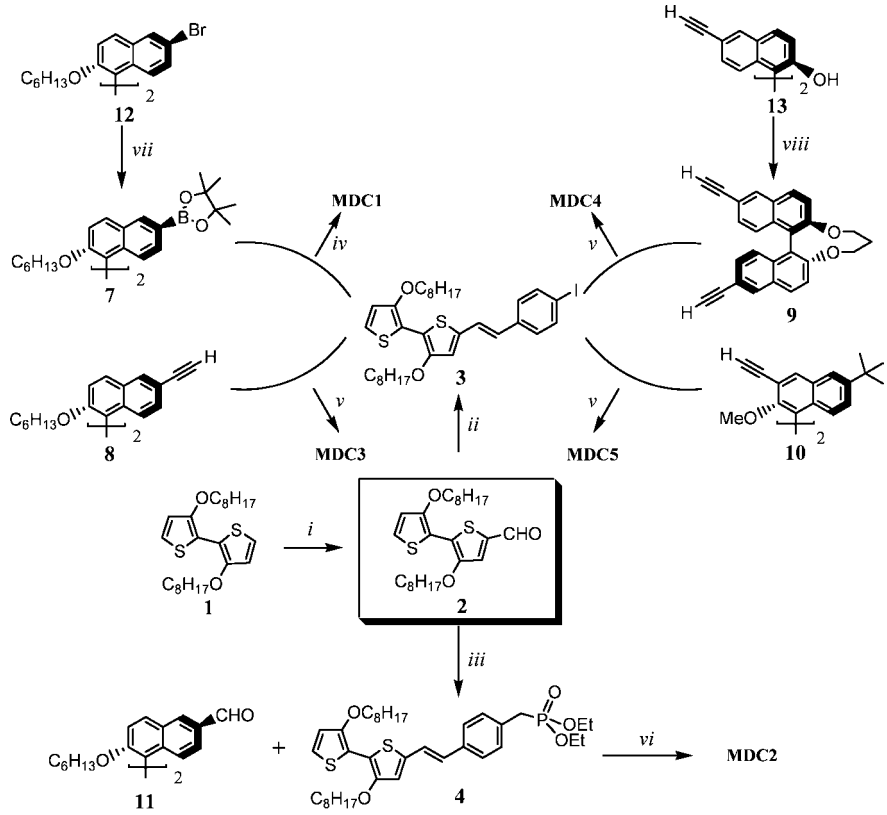


6

The iodo- and diethylphosphonate-functionalized bithiophene units **3** and **4** were prepared by a Wittig–Horner reaction on the aldehyde **2** with **5** and **6**, respectively. The single bond linkage in **MDC 1** was introduced by a Suzuki cross-coupling. It is worth noting that a Stille coupling with the corresponding stannylated binaphthalene derivative was not successful. In **MDC 2**, the double bond was obtained via a Wittig–Horner reaction. Finally, the triple bond in **MDC 3–5** was introduced through a Sonogashira coupling. The binaphthalene derivatives **8**, **10**, **11**, **12** and **13** were synthesized as described in the literature.[20–24] The preparation of the bis(pinacolato)diboronic binaphthalene **7** required the dilithiation of **12** with *n*-BuLi and a subsequent quenching

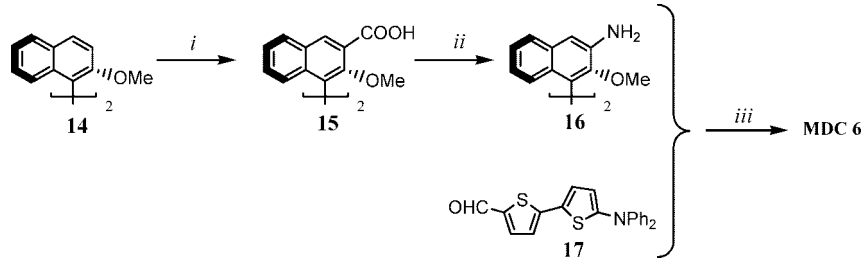
(29) Meille, S. V.; Farina, A.; Bezziccheri, F.; Gallazzi, M. C. *Adv. Mater.* **1994**, *6*, 848.

Scheme 1. Synthesis of the Chiral Λ-Type Oligothiophenes without a DπA Structure (MDC 1–5)[a]



[a] Conditions: (i) (1) DMF, $POCl_3$, dichloroethane, (2) NaOAc (1 M); (ii) NaH, THF, (iii) NaH, THF, (iv) $Pd(PPh_3)_4$, K_2CO_3, H_2O/THF; (v) $Pd(PPh_3)_4$, CuI, diisopropylamine/THF (1/1); (vi) NaH, THF; (vii) (1) *n*-BuLi, THF, −78°C, (2) $B(OMe)_3$, (3) H_3O^+, (4) pinacol, $MgSO_4$, toluene; (viii) NaH, NaI, 1,3-dibromopropane, DMF.

Scheme 2. Synthesis of the Chiral Oligothiophenes with a DπA Structure MDC 6[a]



[a] Conditions: (i) (1) *n*-BuLi, TMEDA, Et_2O, (2) CO_2; (ii) (1) $(PhO)_2PON_3$, NEt_3, (2) H_2O; (iii) molecular sieve (4Å), CH_2Cl_2.

with trimethylborate. Hydrolysis generated the boronic acid binaphthalene derivative, which was immediately converted to the stable pinacol esterified product **7**. Finally, the cyclic binaphthyl-diether **9** was prepared by a nucleophilic substitution of **13** with 1,3-dibromopropane and NaH in DMF in 46% yield.

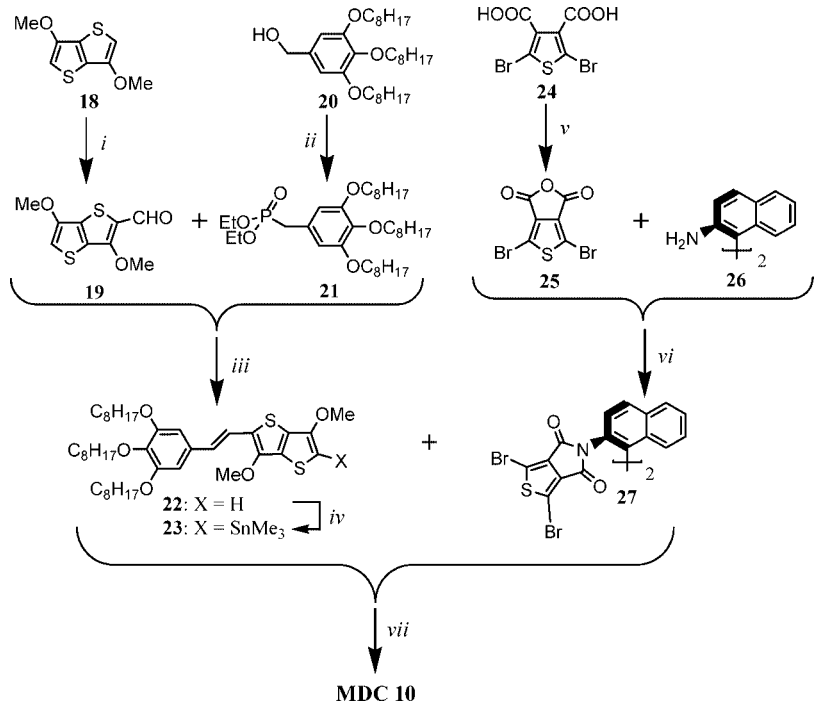
With regard to the preparation of the chiral Λ-type oligothiophenes with a DπA structure, only the synthesis of **MDC 6** is outlined in Scheme 2. The syntheses of the other model compounds (**MDC 7–9**) as well as the building blocks have already been published by Rose et al.[31]

MDC 6 was prepared by an imine formation under standard conditions of diamine **16** with aldehyde **17** in the presence of molecular sieve in 31% yield. **16** was obtained by a Curtius rearrangement of the corresponding dicarboxylic binaphthalene derivative **15**, that in turn could be synthesized after a selective ortholithiation of **14** in the 3-position with *n*-BuLi/TMEDA and a subsequent quenching of the dilithium salt with CO_2 gas before hydrolysis.[25]

Chiral X-Type Oligothiophene. The synthesis of the chiral X-type oligothiophene (**MDC 10**) is presented in Scheme 3. As building block for the oligothiophene, a more planar thienothiophene unit, substituted with electronrich methoxy groups, was chosen instead of a pure thiophene unit to really ensure an efficient conjugation and a facile oxidation. The oligothiophene derivative was end-capped with 3,4,5-tri-

(30) Spencer, H. J.; Skabara, P. J.; Giles, M.; McCulloch, I.; Coles, S. J.; Hursthouse, M. B. *J. Mater. Chem.* **2005**, *15*, 4783.
(31) Zrig, S.; Koeckelberghs, G.; Verbiest, T.; Andrioletti, B.; Rose, E.; Persoons, A.; Asselberghs, I.; Clays, K. *J. Org. Chem.* **2007**, *72*, 5855.

Scheme 3. Synthesis of the Chiral X-Type Oligothiophene (MDC 10)[a]



[a] Conditions: (i) (1) DMF, $POCl_3$, dichloroethane, (2) NaOAc (1 M); (ii) (1) PPh_3, NBS, CH_2Cl_2, (2) $P(OEt)_3$; (iii) NaH, THF; (iv) (1) *t*-BuLi, Et_2O, 0 °C, (2) Me_3SnCl; (v) Ac_2O; (vi) (1) dioxane, (2) Ac_2O; (vii) $Pd_2(dba)_3$, $AsPh_3$, THF.

octyloxyphenyl groups to further lower the oxidation potential and to enhance the solubility.

The thienothiophene **18**[26] was formylated with $POCl_3$/DMF and coupled with phosphonate **21** through a Wittig–Horner reaction. A final stannylation of **22** with trimethyltin chloride led to **23**. In parallel, the tetrabrominated phthalic imide **27** was prepared from the condensation of the commercially available chiral diamine **26** with the carboxylic anhydride **25**. The latter was obtained from the corresponding dicarboxylic derivative **24**.[28] Finally, a 4-fold Stille reaction of **23** with **27** generated **MDC 10**.

Surprisingly, ^{1}H NMR spectroscopy could not validate the structure of this model compound. Different deuterated solvents such as $CDCl_3$, CD_2Cl_2, $C_2D_2Cl_4$, C_6D_6, and DMSO, combined with heating and cooling experiments always resulted in very poorly resolved spectra. IR spectroscopy indicated however the presence of the phthalic imide groups (1747 and 1704 cm^{-1}, respectively, the asymmetrical and symmetrical *C*═O stretchings) and the octyloxy groups (2918 and 2851 cm^{-1}, corresponding to C−H stretchings). To really confirm the 4-fold Stille reaction, MALDI-TOF mass spectroscopy was performed, which indicated the presence of the tetrasubstituted model compound. An estimation of its purity could be obtained through gel permeation chromatography (GPC), where only one narrow elution peak was observed, corresponding to the molecular weight of the model compound (based on the calibration with polystyrene standards). To further confirm the compound's purity, we tried to determine the melting point, but unfortunately, differential scanning calorimetry (DSC) revealed no melting peak; only a glass transition around 18 °C was observed.

Chiroptical Properties. *Chiral* Λ*-Type Oligothiophenes.* To adequately model the interchain interactions of conjugated polymers with optically active side chains in oxidized state, the model compounds should exhibit a similar chiroptical behavior as these polymers in the neutral state. Therefore, a thorough investigation of the chiroptical properties of **MDC 1–9** in neutral state in, respectively, chloroform (**MDC 1–5**) and THF/NEt_3 (**MDC 6–9**) was performed by means of UV–vis and CD spectroscopy.

The UV–vis spectra of the chiral Λ-type oligothiophenes without a DπA structure **MDC 1–5** (Figure 2A) reveal two main absorptions. The first, broad absorption band around 430 nm corresponds to the $\pi-\pi^*$ transition of the oligothiophene moiety in conjugation with the binaphthalene unit. This absorption band shows a clear bathochromic shift by going from a single (425 nm), to a triple (434 nm), to a double (439 nm) bond linkage, corresponding to an increased conjugation. In **MDC 1**, the conjugation between the oligothiophene moiety and the binaphthalene unit is disrupted at the single bond linkage due to steric interactions that pull both moieties out of plane. Further, a more effective electron delocalization is observed through a double bond (**MDC 2**) than through a triple bond (**MDC 3**). The second absorption located around 250 nm can be ascribed to the binaphthalene unit. Only the onset is given because of the absorption interference of the solvent chloroform below 250 nm.

The CD spectra, however, show a different chiral response within these two absorption bands (Figure 2B). The $\pi-\pi^*$ absorption band exhibit a positive monosignate Cotton effect (except for **MDV 5**) with a dissymmetry factor for absorption g_{abs} ($= \Delta\epsilon/\epsilon$) ranging 1×10^{-5}. This effect can be related to a previous study concerning a terthiophene with pendant

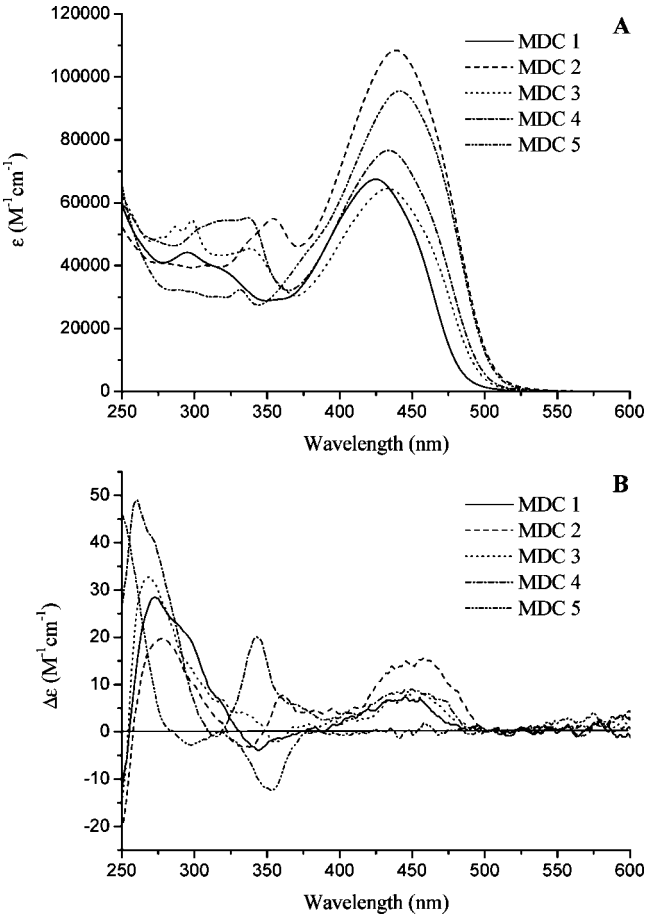


Figure 2. UV–vis (A) and CD (B) spectra of **MDC 1–5** in chloroform.

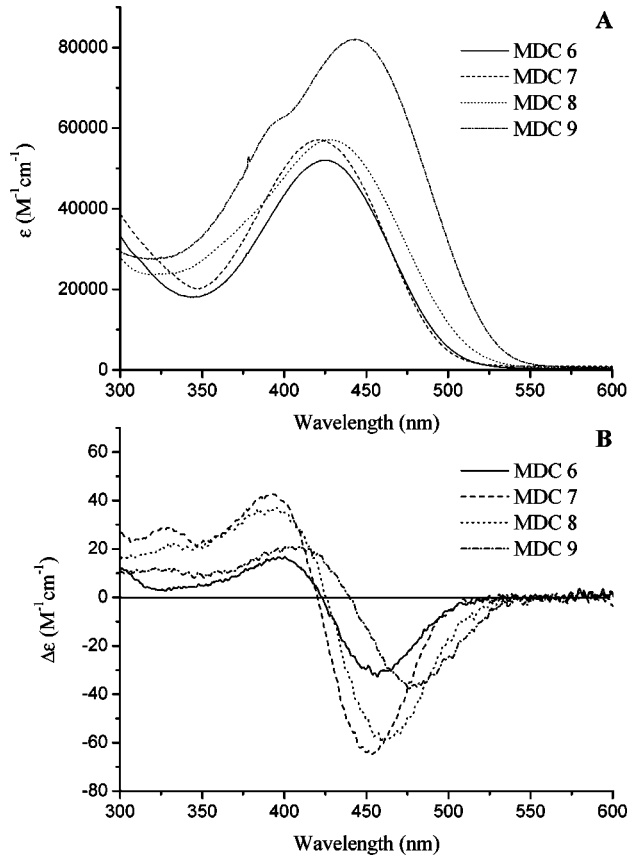


Figure 3. UV–vis (A) and CD (B) spectra of **MDC 6–9** in THF/NEt_3 (99/1).

stereocenters, for which a monosignate Cotton effect of the same order in magnitude was observed.[16] This chiroptical response is thus based on a transfer of chirality from the chiral binaphthalene unit toward the (achiral) oligothiophene moiety. The absorption band of the binaphthalene unit however, exhibits a bisignate Cotton effect (only a positive first Cotton effect is visible, because of absorption interference of chloroform) with a g_{abs} around 1×10^{-4}. This is one order of magnitude higher and is in full agreement with the theory of chiral exciton coupling. Here, the chiroptical response originates from the chiral coupling between the electric-dipole transition moments of the two naphthalene moieties.

The UV–vis spectra of the chiral Λ-type oligothiophenes with a DπA structure **MDC 6–9** exhibit the same main absorption bands (Figure 3a). Here, an analogous bathochromic shift of the $\pi-\pi^*$ transition is also observed by extending the oligothiophene moiety.

The CD spectra of **MDC 6–9** however, drastically differ from those of **MDC 1–5**. The $\pi-\pi^*$ absorption band now reveals a clear bisignate Cotton effect with a g_{abs} around 1×10^{-3}. As in the case of the bisignate Cotton effect within the binaphthalene absorption band, this chiroptical response originates now from the chiral exciton coupling between the two oligothiophene moieties.

The crucial question why **MDC 1–5** do not show such a bisignate Cotton effect within the $\pi-\pi^*$ transition requires a deeper investigation of the chiral exciton coupling. This chiroptical phenomenon is in fact a combination of two interactions, exciton coupling and a chiral interaction, whose magnitudes are given, respectively, by the Davydov splitting (ΔE) and the rotational strength (R)[32]

$$\Delta E = \frac{(\vec{\mu}_1^*\vec{\mu}_2^*)|\vec{R}|^2 - 3(\vec{\mu}_1^*\vec{R})(\vec{\mu}_2^*\vec{R})}{4\pi\epsilon_0|\vec{R}|^5} \quad (1)$$

$$R = \frac{2\pi E_0}{4h}\vec{R}(\vec{\mu}_1^* \times \vec{\mu}_2^*) \quad (2)$$

$\vec{\mu}_{1,2}^*$ are the electric-dipole transition moments of the two chiral oriented oligothiophenes, $\vec{R}$ is the distance vector between the centers of $\vec{\mu}_{1,2}^*$ and E_0 is the excitation energy of the uncoupled system. These expressions reveal two geometrical parameters that can be assigned to the structure of the model compound: the angle and the distance $\vec{R}$ between $\vec{\mu}_1^*$ and $\vec{\mu}_2^*$. Both expressions show a different angle dependency for $\vec{\mu}_{1,2}^*$ and a more pronounced dependency of $\vec{R}$ for the exciton coupling.

To experimentally verify the influence of the angle between $\vec{\mu}_{1,2}^*$ on the chiral exciton coupling, the CD effects of **MDC 3** were compared to those of **MDC 4**. The cyclic diether bridge within **MDC 4** drastically changes the angle

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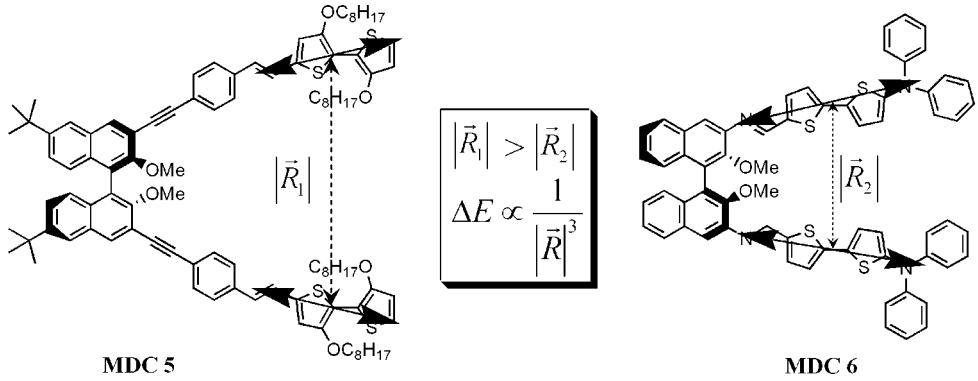

Figure 4. Qualitative picture of the electric-dipole transition moments within **MDC 5** and **MDC 6**.

between $\vec{\mu}^*_{1,2}$ with respect to **MDC 3**, but it does not invoke the desired chiral exciton coupling. Therefore, the absence of a bisignate Cotton effect does not seem to be a matter of angle, but rather a case concerning the $\vec{R}$ parameter.

This can further be proven by comparing the CD effects of **MDC 5** with those of **MDC 6**, both substituted at the 3-position of the binaphthalene unit. Clearly, the DπA system within **MDC 6** seems to be playing a crucial role in obtaining chiral exciton coupling. The electric-dipole transition moment in a DπA system reaches from donor to acceptor. Consequently, the centers of $\vec{\mu}^*_{1,2}$ in **MDC 6** are lying close to each other (Figure 4). In **MDV 5**, no DπA system is present and the electric-dipole transition moments are mainly located on the bithiophene, much further from each other. Keeping in mind that the exciton coupling is inversely related to the third power of $\vec{R}$ (expression 1), it can be assumed that in the case of the chiral Λ-type oligothiophenes without DπA structure (**MDC 1–5**), the distance is too large for a possible exciton coupling to occur.

To further validate our assumption concerning the $\vec{R}$ parameter, the chiral exciton coupling of the series of chiral DπA Λ-type oligothiophenes with different number of thiophenes was compared. According to expression 1, the magnitude of the (chiral) exciton coupling decreases by extending the oligothiophene moiety, because the centers of $\vec{\mu}^*_{1,2}$ will gradually lie further from each other, making $\vec{R}$ larger. Therefore, the $g_{abs}{}^{max}$ values of the chiral DπA Λ-type bi- (**MDC 7**), quater- (**MDC 8**), and sexithiophene (**MDC 9**) were plotted in function of the number of thiophene units (Figure 5). From this plot, it is clear that the $g_{abs}{}^{max}$ value decreases by extending the length of the oligothiophene, which proves that the parameter $\vec{R}$ plays a major role in invoking chiral exciton coupling.

These results impose important restrictions on chiral Λ-type oligothiophenes as study model for optically active conjugated polymers. First, since electronwithdrawing linkages, such as an imine bonding, are required for (chiral) exciton coupling, the ability for oxidation is limited because they significantly raise the oxidation potential of the oligothiophene. Likewise, such an electronacceptor induces an undesired asymmetry within the $\pi-\pi^*$ transition dipole moment, which does not exist within the analogous chiral conjugated polymers. Second, since the g_{abs} value steadily

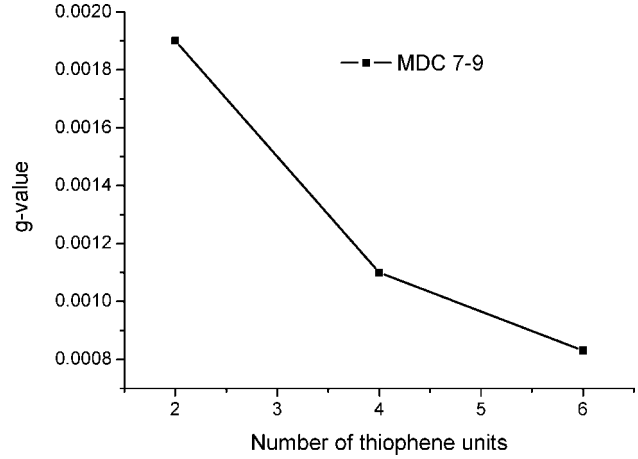

Figure 5. Dependency of $g_{abs}{}^{max}$ as a function of the number of thiophene units for **MDC 7–9**.

decreases with the length of the oligothiophene unit, such chiral Λ-type oligothiophenes have elongation restrictions.

Chiral X-Type Oligothiophene. To overcome the aforementioned drawbacks, we developed a new, oxidizable, chiral X-type oligothiophene (**MDC 10**), which structure resembles the chiral superstructure of conjugated polymers with optically active pendant side chains. This chiral, cruciform-like model compound constitutes a further optimization of chiral exciton coupling with two chiral oriented conjugated systems, since both formulas (1) and (2) predict a maximal interaction for the case that $\vec{R}$ is perpendicularly oriented to $\vec{\mu}^*_{1,2}$. Consequently, the centers of the transition dipole moments need to lie above each other, which is more or less the case in **MDC 10.**

The UV–vis spectrum shows two main absorptions around 480 and 250 nm which can be ascribed to the oligothiophene moiety and the binaphthalene unit respectively (Figure 6A). The $\pi-\pi^*$ absorption band exhibit a defined vibrational fine structure, which indicates a sort of rigidification within the model compound. This can be attributed to possible π-stacking between the oligothiophene moieties, which also recently has been observed for other (achiral) cruciform-like structures.[33–36]

The CD spectrum in turn reveals a clear bisignate Cotton effect in the π-π^* transition with a g_{abs} around 1×10^{-3}, indicative of chiral exciton coupling between the two oligothiophene units. To investigate whether the observed chiral exciton coupling is intramolecular (between two

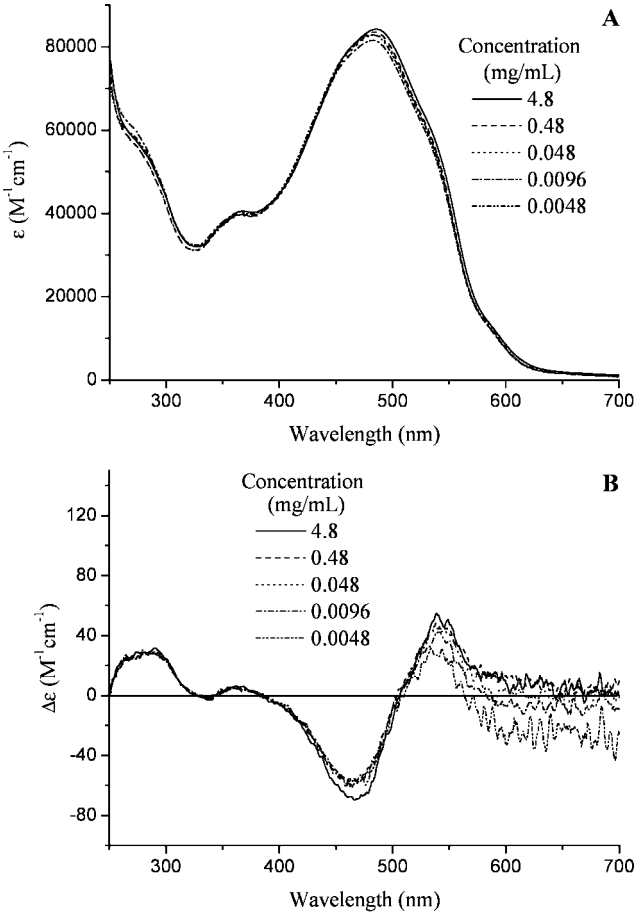

Figure 6. UV–vis (A) and CD (B) spectra of **MDC 10** in chloroform for different concentrations.

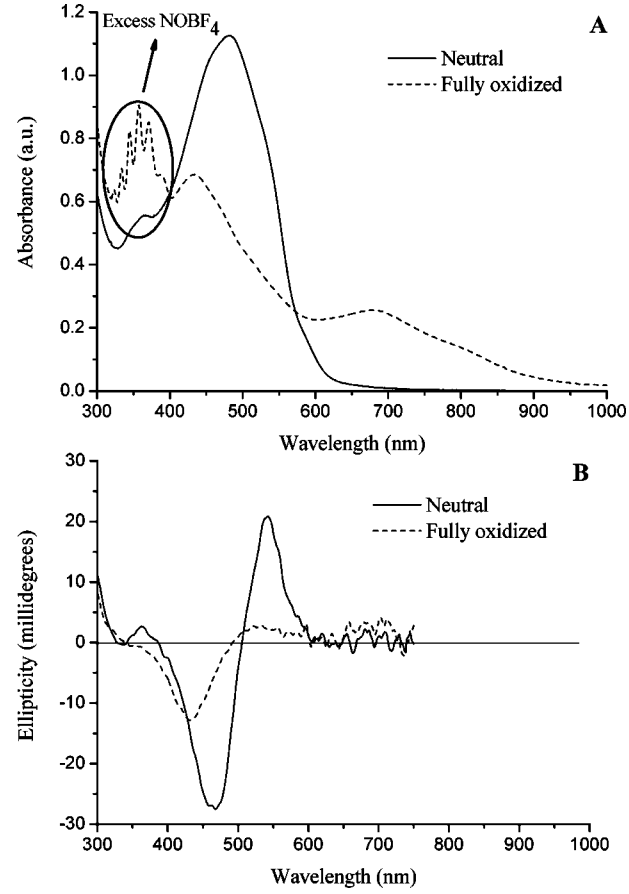

Figure 7. Qualitative UV–vis (A) and CD (B) spectrum of **MDC 10** in chloroform, both in neutral and fully oxidized state (oxidation was performed by $NOBF_4$).

oligomers within one binaphthalene compound) or intermolecular (between two oligomers of two different binaphthalene molecules) in nature, a dilution experiment was performed. From Figure 6B, it is clear that the bisignate Cotton effect is concentration-independent over a wide dilution range (a factor of thousand) and can be assigned to the chiral orientation of the conjugated oligomers by one chiral binaphthalene moiety.

This concentration-independency, even at a typical ^1H NMR concentration (~4.8 mg/mL), in both UV–vis and CD spectrum can further rule out any type of intermolecular aggregation in the NMR experiments. The very poor resolution of the ^1H NMR spectra is thus an intrinsic feature of the model compound itself and not due to aggregation.

As already indicated, the chiral compounds were synthesized as model compounds for chiral conjugated polymers in both neutral and oxidized state. Despite the presence of an electronwithdrawing phthalic imide group, the oligomers could be oxidized by $NOBF_4$ thanks to the electrondonating effect of the methoxy and octyloxy groups.

Upon oxidation, a hypso- and hypochromic shift of the π-π^* absorption band is observed in the UV–vis spectrum, together with the appearance of a new (polaronic) oxidation band around 700 nm (Figure 7A). The corresponding CD spectrum reveals a negative monosignate Cotton effect with a g_{abs}^{max} of 1.5×10^{-3}, located at 434 nm, corresponding to a new π-π^* transition (Figure 7B). Within the wavelength limits of our commercially available CD spectrophotometer, no clear CD spectrum in the polaron band could be measured. However, future research with respect to a controlled chemical and electrochemical oxidation on different types of chiral X-type oligothiophenes with and without an electronwithdrawing phthalic imide function, shall enable us to clarify the chiroptical properties into more detail.

Conclusions

In this work, a conclusive chiral model that can give fundamental insight in the chiroptical properties of conjugated polymers with optically active side chains in both neutral and oxidized state is presented. First, the class of chiral Λ-type oligothiophenes was expanded, and a crucial element was found to model the interchain chiral exciton coupling. The Achilles' tendon embraces the linkage between the oligothiophene and the chiral unit, which indirectly affects the critical distance between the centers of the electric-dipole moments of the two chiral oriented oligothiophenes. We experimentally stated that electronacceptor linkages such as

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an imine bond are required to obtain the desired chiral exciton coupling. The electronwithdrawing nature of these linkages limits, however, the ability of oxidation. Moreover, a steady decrease of the chiral exciton coupling was observed by extending the oligothiophene moiety, which in turn imposes elongation restrictions within these chiral Λ-type models. To overcome all these drawbacks, we designed a new chiral X-type oligothiophene, wherein the crucial distance between the oligothiophenes is reduced to a minimum. As expected, this model compound showed a clear bisignate Cotton effect in chloroform solution due to intramolecular chiral exciton coupling. Combined with the additional ability of oxidation, this chiral model forms the base of our future research toward elucidating the chiral interactions in the oxidized state.

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