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Chirally Organized Oligothiophenes: Towards Modeling Interchain Interactions Within π-Conjugated Systems

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Research in the field of conjugated polymers and oligomers is driven on the one hand by the optimization of the intrinsic molecular features of the conjugated system itself, and on the other hand by the fine-tuning of the intermolecular interactions between the conjugated segments.[1] These intermolecular interactions play a crucial role in the properties of conjugated materials, not only in the neutral but also in the oxidized state. Several oligomeric model compounds, composed of stacked oligothiophenes, have recently been prepared to model the intermolecular π dimerization upon oxidation.[2] This π-dimer formation has even been used as the driving force for molecular actuators, which are composed of tweezer-like oligothiophenes with flexible molecular hinges.[3] Finally, chirality has also been implemented in conjugated models, which has created the possibility of visualizing the induced conformational changes through chiroptical techniques.[4]

The present approaches to monitor the strength of the intermolecular interactions and their dependence on external stimuli, such as oxidation, typically focus on the spectral changes of the oligomers induced by the interaction. However, such studies are usually severely impeded by the fact that both the interaction and the external stimulus affect the electronic properties of the oligomer. Indeed, if oxidation is taken as an example, oxidation results in both the appearance of new, (bi)polaronic bands attributable to the altered electronic structure and (blue)shifts, originating from π dimerization, that is, the interaction.[2,3,5] Moreover, the magnitude and nature of the spectral changes do not only depend on the strength of the particular interaction (such as π interaction or π dimerization), but also on the oligomer itself and the external stimulus (such as oxidation or deprotonation). Therefore, the present studies remain typically focused on a comparison of the spectral changes induced by the same external stimulus (e.g., oxidation) in an analogous series of oligomers.

In contrast, a more general protocol can be obtained if two oligomers are attached to a flexible hinge molecule and if the relative orientation of the two parts of this hinge is monitored, because in that case the spectral changes do not depend on the particular oligomer or external stimulus. Indeed, external stimuli such as oxidation can alter the interaction and, consequently, the distance between the two oligomers held together by the molecular tweezer. The change in this distance is translated to an altered relative orientation and the distance of the two parts of the flexible hinge is also altered (Figure 1). Finally, these changes can conveniently be monitored by, for instance, circular dichroism (CD) spectroscopy. As a consequence, this protocol is not limited to studying differences in interactions within the same class of molecules, but it can, in principle, generally be used for comparing totally different molecules and interactions, provided that the same linking group (e.g., ethenylene group) and oligomers of similar bulkiness and rigidity are employed.

A survey of the molecules studied is shown in Figure 1. As a flexible, chiral linker, a binaphthalene moiety (BN) was used. An overall X-type geometry of the oligomers was preferred because this results in the strongest intermolecular interactions.[6] All model compounds were prepared by a Wittig–Horner reaction of (*S*)-1,1'-binaphthalene-2,2'-dialdehyde with different phosphonated oligothiophenes in a *trans*-selective configuration, as evidenced by ^{1}H NMR spectroscopy.[7] To verify whether the conformation as shown in Figure 1 is indeed possible, some Hyperchem simulations were performed on **MDC 2**. These calculations revealed that the proposed sandwich-like conformation is energetically favored.[7]

The CD spectrum of a chiral BN is composed of a bisignate couplet(s), the intensity (and sign) of which depend on the dihedral angle (θ), the strength of the transition dipole moment, and the orientation of these transition dipole mo-

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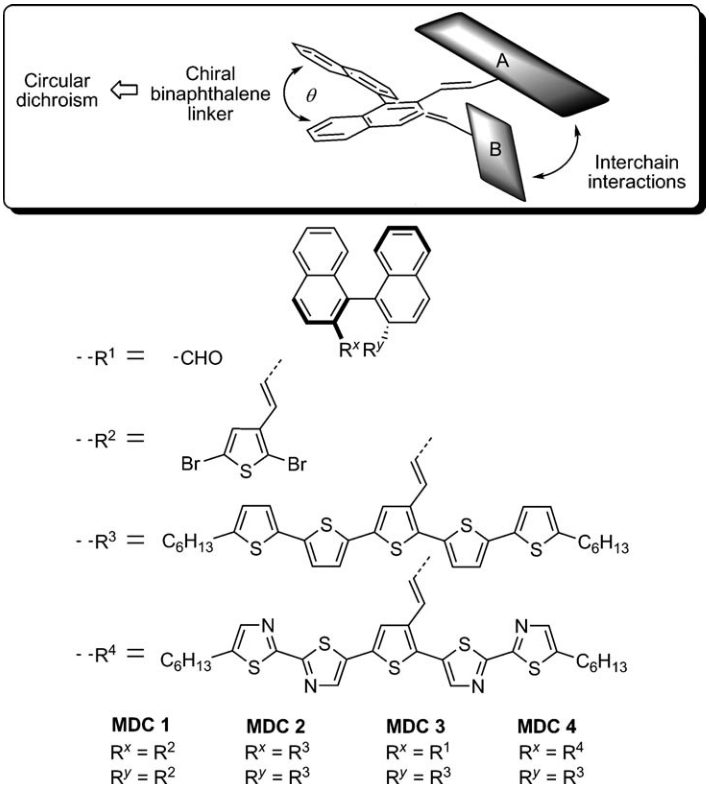

Figure 1. General protocol and the structure of **MDC 1–4**.

ments with respect to the naphthalene axis.[8] In particular, the high-energy lobe of the CD signal in a typical (*S*)-BN geometry evolves from a small positive to a strong negative effect, with a zero-crossing at approximately 110° and a moderate signal at approximately 90°, the typical angle of most BN molecules.[8] By further decreasing θ, the intensity again drops (Figure 6). Note that the dihedral angle can vary over a broad range and even adopt small values, provided that an additional driving force, such as incorporation into a ring, is present.[9] Consequently, probing this CD signal can be used to visualize changes in the dihedral angle of the BN core and, hence, interactions between the oligomers and even qualitatively compare them,[10] provided that following requirements are fulfilled:

1) The tracked signal must solely originate from the BN couplet, that is, it may not interfere with signals from the oligomer. A comparison of the UV/Vis and CD spectra of **MDC 1** and the oligothiophene reveals that indeed overlapping occurs.[7] However, when $\lambda > 380$ nm, **MDC 1** does not give any signal and the UV/Vis and CD spectra are exclusively governed by the oligomer. On the other hand, for $280 < \lambda < 320$ nm, in which the shape of the CD spectra of **MDC 1** and **MDC 2** coincide and the chromophores hardly absorb, the Cotton effects solely arise from the BN hinge molecule. Therefore, $\Delta\varepsilon$ at the minimum of the lobe near 310 nm, denoted as $\Delta\varepsilon_{BN}$, can be monitored as the indicative signal.
2) The CD signal must not be affected by variations in the strength or orientation of the monitored transition dipole moment. Although substituents can indeed influence the orientation, this effect is only important for quantitative studies and can therefore be neglected.[8]

Concerning the influence of changes in ε, it might be speculated that oxidation could affect ε and, hence, the CD response as it changes the electronic properties of the oligothiophene and introduces additives. Therefore, **MDC 3** was oxidized by gradual addition of Meerwein's salt (Et_3OSbCl_6). This oxidant was chosen because it has been shown to result in a one-electron oxidation of oligothiophenes without any other side reaction.[3,11] The UV/Vis spectra (Figure 2c) show that oxidation of the oligothiophene indeed occurs, but, importantly, the Cotton effect near 320 nm is not affected. Therefore, possible changes of $\Delta\varepsilon_{BN}$ of **MDC 2** and **MDC 4** upon oxidation cannot be due to an altered orientation or strength of the transition dipole moment of the monitored BN transition, but must originate from a different dihedral angle.

Next, **MDC 4**, in which an electron-poor oligothiazole and the pentathiophene are stacked, was subjected to oxidation. Owing to the electron poverty of oligothiazole, only oxidation of the oligothiophene is possible, which is again visualized in the UV/Vis spectra. Importantly, $\Delta\varepsilon_{BN}$ decreases upon oxidation, revealing a decline in the dihedral angle and, hence, a change in the interaction between the conjugated pentamers.[12] Note that **MDC 4** shows a clear bisignate Cotton effect near 400 nm, which originates from chiral exciton coupling between the two oligomers and is therefore absent in **MDC 3**, which is equipped with only one oligomer. In this way, the BN moiety transfers its chirality to the oligothiophenes. Finally, **MDC 2**, which is composed of two oxidizable pentathiophenes, is oxidized. From the UV/Vis spectra, it can be concluded that oxidation indeed occurs and that at higher degrees of oxidation, additional, blue-shifted peaks (near 650 and 950 nm) arise, which can be attributed to π dimerization.[2,3,5] A second indication of interactions between the oxidized oligothiophenes is provided by cyclic and differential-pulse voltammetry (Figure 3).[13] The cyclic voltammogram of **MDC 2** shows two quasireversible oxidations. In the case of **MDC 4** one quasireversible oxidation is present together with an irreversible second oxidation at higher potential, which can be attributed to the instability of an oxidized oligothiazole moiety. The first oxidation of **MDC 2** clearly occurs at a lower potential than the first oxidation of **MDC 4**, showing that the oxidized pentathiophene is more stabilized by a pentathiophene (**MDC 2**) than by an oligothiazole (**MDC 4**). This observation clearly demonstrates the interaction between the (oxidized) oligothiophenes.

Oxidation also affects the CD spectra. Moreover, the clear absence of an isosbestic point is in agreement with two subsequent one-electron oxidations (one on each pentathiophene), the latter being accompanied by π dimerization. This is in contrast with the single-step oxidation of **MDC 4**,

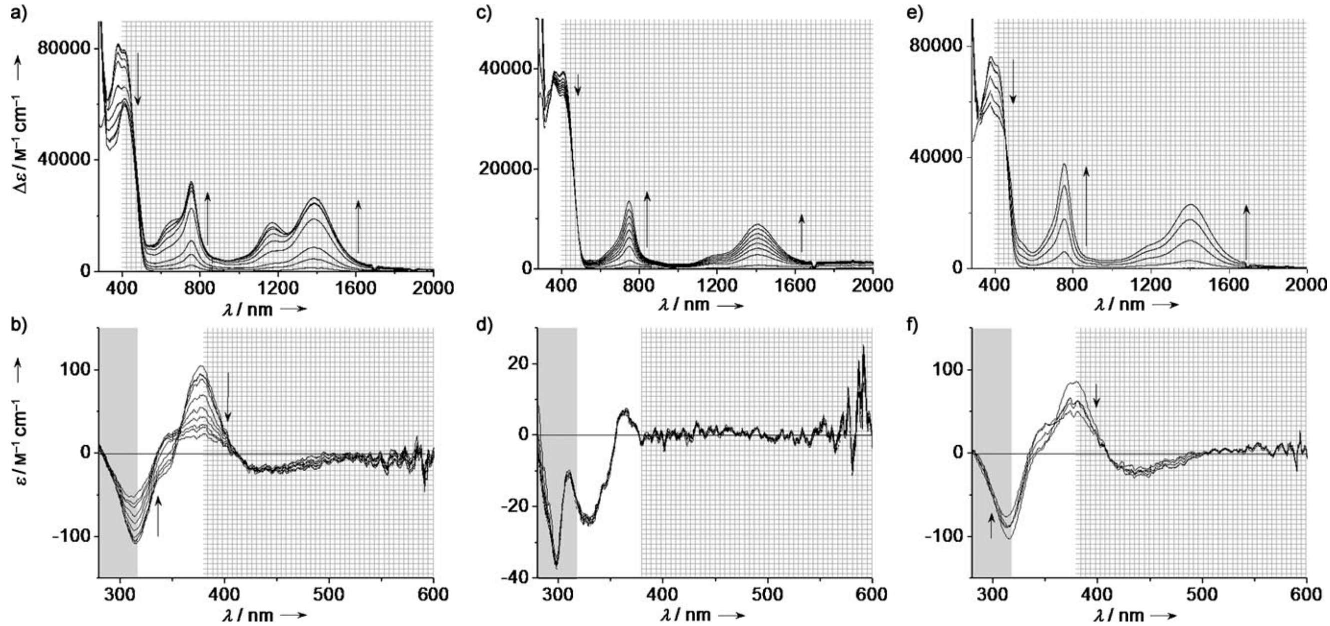

Figure 2. UV/Vis and CD spectra of **MDC 2** ($c=1.47.10^{-5}$ M) (a, b), **MDC 3** ($c=3.94.10^{-5}$ M) (c, d), and **MDC 4** ($c=3.13.10^{-5}$ M) (e, f) in dichloromethane during gradual oxidation with Et_3OSbCl_6. In the region $280<\lambda<320$ nm, indicated by the grey areas, the CD signals originate from the BN hinge; in the region $\lambda>380$ nm, indicated by the checked areas, the UV/Vis and CD spectra arise from the oligomer. See the Supporting Information for more detailed spectra.

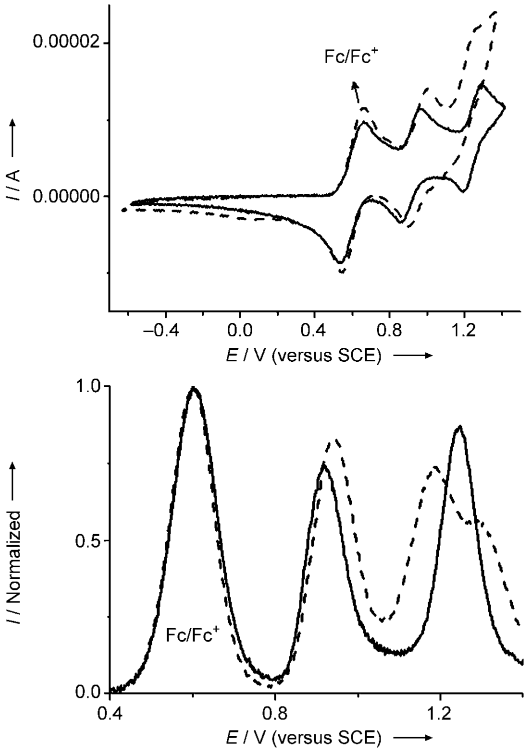

Figure 3. Calibrated cyclic voltammograms (top) of **MDC 2** (-----) and **MDC 4** (——) in dichloromethane with ferrocene as the internal standard versus a standard calomel electrode (SCE; scan rate = 100 mV s^{-1}). Calibrated and normalized differential pulse voltammograms (bottom) under the same conditions, but with a pulse amplitude of 75 mV (50 ms) and a scan rate of 20 mV s^{-1}.

in which such an isosbestic point can be observed. Finally, the comparison of the magnitude of the change of $\Delta\varepsilon_{BN}$ of **MDC 2** and **MDC 4** reveals that the interaction between oxidized pentathiophenes (although both are electron poor and charged) is much stronger[12] than the interaction between oxidized pentathiophene and electron-poor but neutral oligothiazole, which clearly reflects the strength of the π dimerization.

As already mentioned, the magnitude of $\Delta\varepsilon_{BN}$ directly depends on the interaction between the two moieties (if present) that are connected to the naphthalenes. Therefore, probing $\Delta\varepsilon_{BN}$ cannot only be used to monitor changes in interactions upon oxidation, but it can already reveal differences in π interactions in different neutral oligothiophenes. Indeed, $\Delta\varepsilon_{BN}$ of **MDC 1**, in which no interactions between oligomers are present, is approximately 60 M^{-1} cm^{-1},[7] whereas in contrast, $\Delta\varepsilon_{BN}$ of **MDC 2** and **MDC 4** are approximately 100 M^{-1} cm^{-1}, indicating a smaller θ and thus reflecting the π-interactions between the oligomers in the latter compounds. Second, because the model does not rely on the chiroptical properties of the oligomers, it is not restricted to studying π interactions and their differences induced by oxidation, but it can more generally be used to probe any interaction between moieties connected to the binaphthalene core through the same ethenylene linker. To test this hypothesis, **MDC 5–6** (Figure 4) were prepared, in which deprotonation instead of oxidation allows for the manipulation of the interactions between the oligomers.

To confirm that the deprotonation does not wrongly affect $\Delta\varepsilon_{BN}$, KO*t*Bu is first gradually added to **MDC 5**. The red shift (from 400 to 440 nm, Figure 5) confirms the depro-

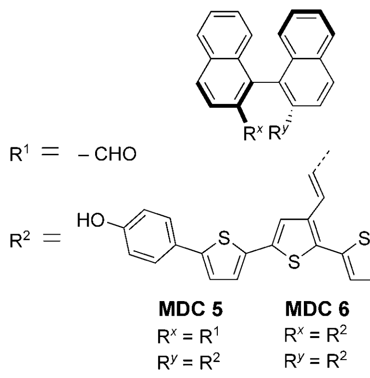

Figure 4. Structures of **MDC 5** and **6**.

tonation of the oligomer, but $\Delta\varepsilon_{BN}$ remains unchanged. This again demonstrates that neither changing the nature of the chromophore nor the introduction of ions influence $\Delta\varepsilon_{BN}$. Aggregation can also be ruled out because **MDC 6** dissolves in *t*BuOH.[7] Moreover, the fact that the CD spectra of **MDC 3** and **MDC 5** are very similar in both shape and magnitude again supports the fact that they are essentially due to the chiral BN, irrespective of the presence and nature of the oligomer. Next, **MDC 6** was subjected to deprotonation, which can be visualized in both the UV/Vis and CD spectra. Interestingly, after deprotonation the original, neutral situation can be restored by the addition of HCl.[7] Furthermore, a more detailed inspection of the spectra reveals that the deprotonation is a two-step process, with the second deprotonation only occurring at large quantities of KO*t*Bu (these spectra are shown in grey, Figure 5). The necessity to use large quantities of the base for the second deprotonation suggests that the deprotonation of the first oligomer significantly decreases the acidity of the second one. This is confirmed by the fact that if the less basic KOH is employed, the second deprotonation does not occur, even at a very large excess. If the CD spectra are considered, it is striking that $\Delta\varepsilon_{BN}$ again amounts to approximately $100\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$ (**MDC 6**). The first deprotonation results in a relatively small drop in $\Delta\varepsilon_{BN}$; the second deprotonation further increases the interactions between the oligomers, which is reflected by the smaller $\Delta\varepsilon_{BN}$ and, hence, θ.[12]

As already mentioned, the universality of the approach allows the qualitative comparison of interactions between a set of two oligomers, because this is reflected by the magnitude of $\Delta\varepsilon_{BN}$. Such a comparison (Figure 6) shows that in the absence of any interactions (**MDC 1**) $\Delta\varepsilon_{BN}$ is approximately $60\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$, corresponding to a typical $\theta \approx 90°$,[8] and π interactions (**MDC 2**, **MDC 4**, and **MDC 6**) decrease θ. The fact that similar values are found ($\Delta\varepsilon_{BN} \approx 100\,\mathrm{M}^{-1}\mathrm{cm}^{-1}$) can be attributed to the fact that the interaction is in all cases the same and/or the $\Delta\varepsilon_{BN}$ to θ relationship reaches a plateau. Both oxidation and deprotonation increase the interactions between the oligomers (θ further decreases), but the (multiple) oxidation increase the interactions to a larger extent than the (multiple) deprotonation.

In conclusion, a protocol that allows (changes in) interactions between two oligomers to be monitored is reported. It consists of the attachment of two oligomers to a chiral, flexible binaphthalene core and monitoring $\Delta\varepsilon_{BN}$. Because this

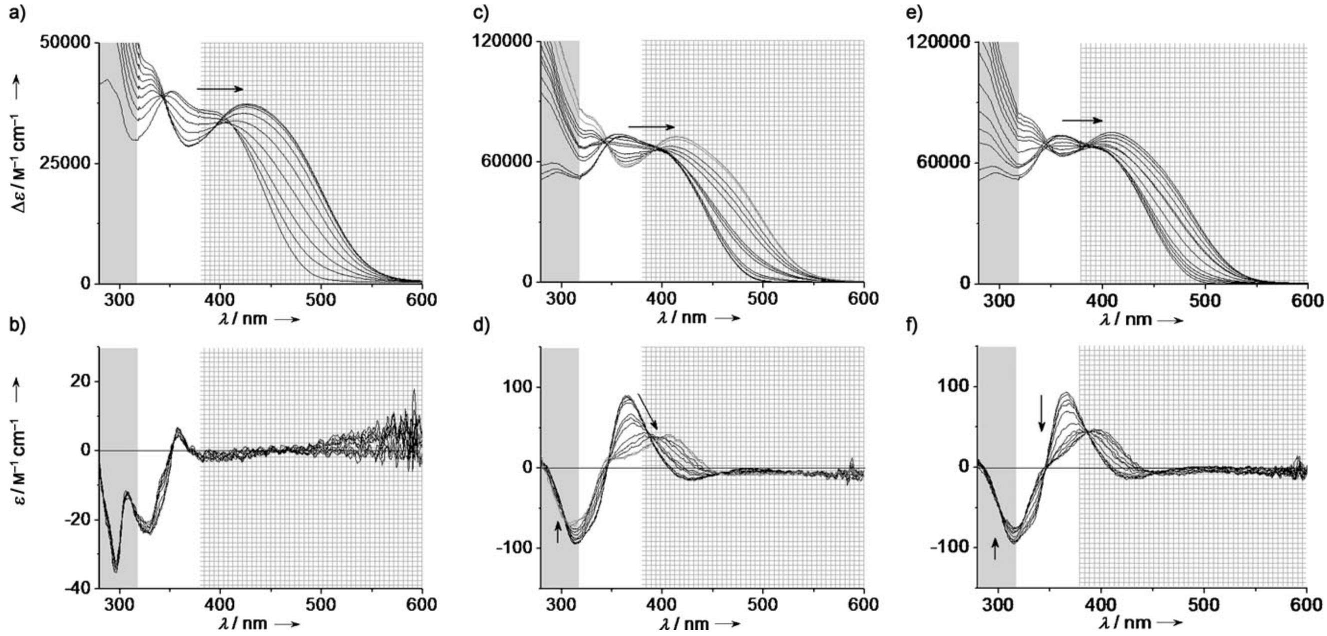

Figure 5. UV/Vis and CD spectra of **MDC 5** ($c = 2.41.10^{-5}\,\mathrm{M}$) (a, b) and **MDC 6** ($c = 2.41.10^{-5}\,\mathrm{M}$) (c, d) in THF/*t*BuOH (1:1) during gradual deprotonation with KO*t*Bu and **MDC 6** ($c = 2.41.10^{-5}\,\mathrm{M}$) (e, f) in THF/MeOH (8:2) during gradual deprotonation with KOH. In the region $280 < \lambda < 320$ nm, indicated by the grey areas, the UV/Vis and CD signals originate from the BN hinge; in the region $\lambda > 380$ nm, indicated by the checked areas, the UV/Vis and CD spectra arise from the oligomer. See the Supporting Information for more detailed spectra.

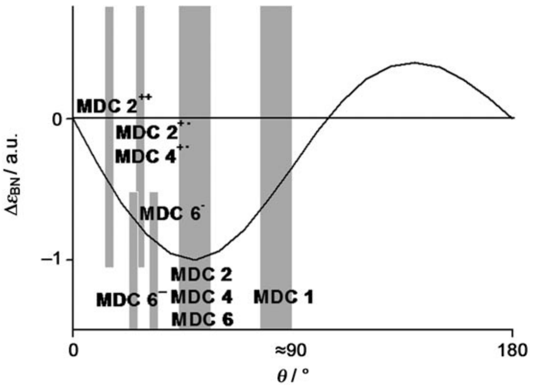

Figure 6. Comparison of the dihedral angle (θ) in the model compounds before and after the external stimulus. The evolution of $\Delta\varepsilon_{BN}$ as a function of θ was calculated by using classical physics, assuming standard binaphthalene geometries, Gaussian absorption bands ($\sigma = 1.5 \times 10^{14}\,s^{-1}$), and a transition dipole strength of 50 D^2 located along the naphthalene long axis.[14]

property is independent of the nature of the oligothiophene or external stimulus performed, it can be generally used to monitor and compare interactions between two π-conjugated oligomers.

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[10] Because Δε does not scale (linearly) with the dihedral angle and the (change of the) dihedral angle does not (linearly) depend on the (change in the) strength of the interaction, and also owing to some simplifications, the proposed model cannot be used to quantitatively measure the strength of the interactions between the oligomers, but only allows the qualitative scaling of interactions between oligomers.

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[12] If θ is such that a maximal CD intensity is obtained, any variation of θ, and, hence, of the interaction between the oligomers (decrease or increase), results in a decline of the CD intensity. Applied to the experiments performed, the drop of the CD intensity upon applying the external stimulus can, in principle, both indicate an increase or decrease of θ, provided that it was started from a maximal CD intensity. However, the nature of the interaction (such as delocalization of charges or π dimerization) and the vast amount of literature on these subjects rules out the possibility that the interaction weakens.

[13] The first and second oxidation, resulting in **MDC 2**$^{+\cdot}$ and **MDC 2**$^{++}$, respectively, occur at a lower potential than oxidation of the parent, uncoupled pentathiophene, which can be attributed to charge delocalization of the radical cation by the second pentathiophene and π dimerization. These results will be published elsewhere.

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