Chiroptical Response Inversion upon Sample Flipping in Thin Films of a Chiral Benzo[1,2-*b*:4,5-*b'*]dithiophene-based Oligothiophene

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A new chiral benzo[1,2-*b*:4,5-*b'*]dithiophene-based oligothiophene has been synthesized and spectroscopically characterized in solution and in solid state. The electronic circular dichroism (ECD) spectra of thin films revealed the occurrence of an uncommon phenomenon, consisting in the inversion of circular dichroism sign by sample flipping. To the best of our knowledge, this is unprecedented in samples, where no preferential preferential orientation of the chromophores had been induced, and must be due to spontaneous local anisotropies. It reveals peculiar features upon usual solvent annealing procedure, but finally results in stable and very strong signals, which are perfectly reproduced in sign, relative and even absolute magnitude. Although the recorded signal cannot be considered a true ECD spectrum, it corresponds to a very large discrimination of light circular polarization, which is well explained by means of the Mueller matrix analysis and does not depend on instrumental defects. It is a genuine property of this material, which correlates with polarized optical microscopy (POM) images and only depends on the self-assembling properties of this molecule. This phenomenon may have relevant implications, on account of its strength and of the interest of oligothiophenes in current optoelectronic devices.

Introduction

Thanks to the possibility to modulate both electronic and optical properties, organic semiconductors based on π -conjugated polymers and oligomers have opened the way to the development of innovative optoelectronic devices. By changing the substituents in a given molecular skeleton, one can modulate properties like charge and exciton transport, absorption and emission spectra, and response to external stimuli. The fundamental electro-optical properties of π -conjugated systems (light absorption and emission, charge transport, exciton transfer, etc.) depend not only on their chemical structure and on the conformation assumed, but also on the supramolecular interactions and the nano/mesoscale organization in the solid-state.¹⁻³ Chirality represents one of the most sophisticated expedients to control the supramolecular aggregation of similar systems (in particular their interchain spacing and/or alignment).⁴⁻⁷ In fact, the introduction of stereodefined chiral groups on the π -conjugated backbone can drive these molecules to organize into chiral supramolecular architectures, where a perfect alignment between proximate π -conjugated chains is disfavoured with respect to a twisted arrangement.⁸⁻¹¹ Such a supramolecular organization, among other things, may reduce

aggregation-induced fluorescence quenching.¹²⁻¹⁴

Moreover, chiral conjugated polymers and oligomers may be used to fabricate sensors capable to discriminate enantiomers,¹⁵ and circularly polarized (CP) light emitters^{16,17} or detectors.¹⁸

The first step to the successful detection of circular polarization of light is the development of molecules or materials which provide active layers with strong discrimination of left vs. right CP-light. To this end, Fuchter and Campbell used an azahelicene, a molecule with reasonable semiconducting properties and at the same time a strong electronic circular dichroism (ECD).¹⁸ Although promising, their approach may suffer from some limitations: in the very first place, currently enantiopure helicenes must be obtained from chromatographic resolution; secondly, it may be difficult to tune electronic properties, like charge/exciton transport and absorption spectrum.

Very recently, Oh *et al.* demonstrated the importance of chiral self assembly in chiroptical sensing, taking advantage of the enhanced ECD allied to self-assembled chiral nanowires of perylene diimides.¹⁹

Following our own interest in chiral supramolecular structures of organic chromophores,^{14,20-22} we thought to work with oligothiophenes, which have well known applications in optoelectronics, and to decorate them with inexpensive chiral

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groups from natural sources, seeking self-assembly properties, which would ensure supramolecular chirality at the nanoscale

Scheme 1. Structure of the (S)-3,7-dimethyl-1-octyl-functionalised BDT-based oligothiophene **1** synthesized in this work.

and the onset of extraordinary optical properties. We found a most peculiar behaviour with a benzo[1,2-*b*:4,5-*b'*]dithiophene derivative, which may open the way to the development of chiral active layers with a new form of CP-light discrimination. Benzodithiophene or BDT, represents a successful motif, owing to its good cofacial π - π stacking in the solid state, promoting charge transport and exciton mobility.²³ Furthermore, the two positions on the central benzene ring can bear substituents (in particular, branched alkoxy chains or further conjugated groups), to ensure good solubility and tune the molecular orbitals energy levels of the resulting molecules.^{24,25} The BDT nucleus is widely used especially as electron-rich building block in donor-acceptor (D-A) copolymers²⁶ and acceptor-donor-acceptor (A-D-A) small molecules²⁷ for organic photovoltaic devices (OPVs), achieving power conversion efficiencies up to almost 10%.^{28,29} Recently, various BDT-based oligothiophenes for high-performance OPVs have been described.³⁰⁻³⁹

We synthesized a new BDT-based π -conjugated system **1** bearing the (S)-3,7-dimethyl-1-octyl group (**Scheme 1**). This chiral branched chain is easily prepared in enantiopure form from an inexpensive natural terpene, it is devoid of functionalities and transfers its asymmetry (centre of chirality at position 3 of the aliphatic chain) to the entire system (supramolecular chiral organisation) exclusively through hydrophobic forces and steric effects.

Electronic circular dichroism (ECD) provides a very convenient way to characterize thin films of chiral π -conjugated molecules, because it responds sensitively to supramolecular chirality and for this reason it can selectively reveal ordered aggregated forms. Very recently, we used localized ECD spectroscopy, i.e. a CD-imaging dubbed CD_i ,⁴⁰ to achieve the imaging of local domains with different order in thin films of chiral π -conjugated polymers.⁴¹

The crude signal resulting from a common ECD spectropolarimeter is the sum of various contributions, which can be well accounted for and disentangled by applying Mueller matrix analysis.⁴² The leading terms of the ECD signal recorded for an anisotropic sample are:⁴³

$$CD_{\text{tot}} \approx CD_{\text{true}} + \frac{1}{2} (LD' \cdot LB + LD \cdot LB') + (LD \cdot \sin \alpha + LB) \cdot \cos 2\theta + \dots \quad (1)$$

where CD_{true} is the genuine CD; LD and LB represent linear dichroism and linear birefringence, respectively, while the prime in $LD' \cdot LB$ and $LD \cdot LB'$ indicates a +45° shift between LD

and LB axes; the θ angle describes the sample rotation around the incident light direction, and α is associated with the residual birefringence of the photoelastic modulator (PEM), i.e. the device used to generate CP radiation. This third term ultimately arises from the current limited technical possibility to realize the “perfect” CD experiment: i.e. the difference between two absorption measurements with oppositely circularly polarized light, free from optics imperfections and from the fact that for most of the time the PEM produces elliptically polarized light (and even linearly polarized one) rather than true CP light. For this reason, this term is definitely to be considered an artifact, related to samples with large macroscopic anisotropies. To take care of this problem, Kuroda *et al.* designed and built a Universal Chiroptical Spectrophotometer (UCS-1: J-800KCM) for obtaining artifact-free ECD spectra of solid-state samples.⁴⁴ At a more basic level, however, simple sample rotation about the optical axis corresponds to changing θ in Equation 1 and allows one to reveal and possibly eliminate this artifact.

Things are very different for the second term in Equation 1, namely $\frac{1}{2}(LD' \cdot LB + LD \cdot LB')$, because it is invariant upon sample rotation and, more importantly, it is completely independent of instrumental faults or by the intrinsic limitation of polarization-modulation measurements, as it is known in the context of chiral nematic systems.⁴⁵ Its peculiarity consists in the fact that by flipping the sample by 180° with respect to the light axis, it becomes exactly inverted. Because it will be the focus of our further discussion, we shall call it simply LDLB.

In our own experience, in most cases films of π -conjugated polymers or oligomers prepared by spin coating or drop-casting and after thermal or solvent annealing do not display severe artifacts, due to macroscopic anisotropies. The absence of macroscopic LD and LB is a direct consequence of the lack of a preferential orientation of the sample.

On the contrary, all the thin films of **1** revealed a strong LDLB effect, which called for an in-depth investigation.

Results and discussion

Synthesis of the (S)-3,7-dimethyl-1-octyl-functionalised BDT-based oligothiophene **1**

The complete synthetic pathway of the (S)-3,7-dimethyl-1-octyl-functionalised BDT-based oligothiophene **1** developed in this work is shown in **Scheme 2**.

First of all, benzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-dione (**2**) was synthesized following a literature procedure:²⁴ commercial 3-thiophenecarboxylic acid (**3**) was converted into the corresponding acid chloride **4** by reaction with oxalyl chloride, followed by treatment with *N,N*-diethylamine to afford the intermediate amide **5**, which was then cyclo-dimerized by means of *n*-BuLi to form **2** with good yield (77%). The latter was reduced to the corresponding diol **6** using NaBH₄ in EtOH (71% yield); it is worth noticing that the subsequent work-up was only possible under acidic conditions, because neutral or alkaline environments led to the isolation of the starting dione **2**. (S)-3,7-Dimethyl-1-bromooctane (**7**) was synthesized by Pd-

Scheme 2. Synthesis of (*S*)-3,7-dimethyl-1-octyl-functionalised BDT-based oligothiophene **1**. Conditions: a) $(\text{COCl})_2$ (2.0 eq.), CH_2Cl_2 , $0^\circ\text{C} \rightarrow \text{r.t.}$, 24 h; b) Et_2NH (2.5 eq.), CH_2Cl_2 , $0^\circ\text{C} \rightarrow \text{r.t.}$, 4 h; c) *n*-BuLi (1.1 eq.), THF, $0^\circ\text{C} \rightarrow \text{r.t.}$, 24 h, then $\text{HCl}_{(\text{aq})}$; d) NaBH_4 (2.0 eq.), EtOH, 5 h, r.t. , then $\text{HCl}_{(\text{aq})}$; e) H_2 , Pd/C, AcOEt, 24 h, r.t. ; f) NBS (1.2 eq.), PPh_3 (1.2 eq.), CH_2Cl_2 , 2 h, 0°C ; g) **7** (2.1 eq.), K_2CO_3 (10.0 eq.), CH_3CN , 85°C , 30 h; h) *n*-BuLi (2.3 eq.), CBr_4 (2.6 eq.), THF, 5 h, $-78^\circ\text{C} \rightarrow \text{r.t.}$; i) **12** (3.5 eq.), K_2CO_3 (3.0 eq.), Ag_2O (2.0 eq.), $\text{Pd}(\text{PPh}_3)_4$ (5 mol%), 1,4-dioxane, 70°C , 90 h.

catalysed hydrogenation of commercial (*S*)-(-)- β -citronellol (**8**) and following bromination of the resulting alcohol **9** with PPh_3 and NBS.⁴⁶

The benzo[1,2-*b*:4,5-*b'*]dithiophene-4,8-diol (**5**) was then alkylated through nucleophilic substitution with a slight excess of the chiral bromide **6** in heterogeneous conditions (K_2CO_3 and acetonitrile), affording the corresponding dialkylated product **10** (88% yield), which was subsequently brominated to give 2,6-dibromo-4,8-bis(((*S*)-3,7-dimethyloctyl)oxy)benzo[1,2-*b*:4,5-*b'*]dithiophene (**11**); this reaction was performed under alkaline conditions with *n*-BuLi and CBr_4 , since a preliminary bromination test of **10** in acidic conditions (NBS in CHCl_3) unfortunately afforded the precursor **2** as main product. Finally, the Suzuki-Miyaura coupling of **11** with an excess of the commercial boronic ester **12**, performed under optimised

conditions ($\text{Pd}(\text{PPh}_3)_4$, K_2CO_3 , Ag_2O , 1,4-dioxane, 70°C), yielded the desired BDT-based oligothiophene **1** (30% of yield).

Following exactly the same procedure, but on a smaller scale, we prepared the enantiomeric compound *ent*-**1**, starting from the non-natural isomer (*R*)-(+)- β -citronellol.

Optical and chiroptical properties of the (*S*)-3,7-dimethyl-1-octyl-functionalised BDT-based oligothiophene **1**

Spectroscopic characterization of the chiral oligothiophene **1** was first conducted in solution, recording UV-Vis absorption, fluorescence and ECD spectra in a “good” solvent such as chloroform (**Figure 1**).

The absorption spectrum showed a prominent broad band between 330 and 500 nm, with an evident vibronic structure and a maximum centred at 432 nm (molar extinction coefficient $\epsilon = 53000 \text{ M}^{-1} \text{ cm}^{-1}$), related to the π - π^* transition

of dialkyloxy-functionalized BDT-based oligothiophenes.⁴⁷ A simulation of the absorption profile run with time-dependent density functional theory (TDDFT) at CAM-B3LYP/TZVP level (including a solvent model for chloroform, see Supplementary Information for details) revealed the presence of three distinct transitions in the range between 270 and 500 nm. Of these, the first and strongest one at 430 nm is long-axis polarized, while the other two at shorter wavelengths are both tilted by $\approx 50^\circ$ with respect to the long axis (**Figure 1d**). This is relevant to interpret LD signals, as discussed below.

The emission spectrum (excited at 382 nm) displayed a broad band between 450 and 650 nm, with maximum around 513 nm and a long-wavelength tailing; therefore, this system showed quite a large Stokes shift (81 nm), with a quantum yield of 28%. The ECD spectrum was very weak and had dissymmetry factors g (defined as $\Delta\epsilon/\epsilon$) always $< 10^{-4}$, indicating that the perturbation exerted on the intrinsically achiral chromophore of **1** by individual chirality centres of the alkyl chains is very small in isolated molecules.⁴⁸⁻⁵⁵

Since it is well-known that, upon addition of a proper non-solvent to a perfectly dissolved sample, π -conjugated polymers and oligomers form supramolecular aggregates in solution (which are expected to mimic the solid-state organization),^{14,20-22} we recorded UV-Vis absorption and ECD spectra of **1** in various solvent mixtures, composed of CHCl_3 as “good” solvent and *n*-hexane, cyclohexane, toluene, ethyl acetate, methanol or ethanol as “poor” solvents (see **Figure S1** in Supplementary Information). Unfortunately, in all cases they showed only negligible differences with the spectra recorded in pure chloroform and no evident relation between the spectral profile and the increasing non-solvent concentration could be found. Therefore, these results revealed that **1** would not undergo aggregation in solution but it directly precipitates in the presence of > 95 vol% of “bad” solvent, preventing further investigation.

Figure 1. UV-Vis absorption (a), fluorescence (b) and ECD (c) spectra of the BDT-based oligothiophene **1** in CHCl_3 . Sample concentration: $1.0 \cdot 10^{-5}$ M; cell length: 1 cm; excitation wavelength: 382 nm. (d) TDDFT-calculated UV spectrum for the model shown (alkyl chains in **1** replaced by methyl groups) and polarization of the main transitions #1-#4.

Figure 2. UV-Vis absorption (a) and ECD (b) spectra of **1** as thin film prepared by drop-casting of a 10^{-2} M solution in CHCl_3 . In panel (b) the red dotted line represents the ECD spectrum recorded from the *front* side, *i.e.* with the solid deposition facing the light source, while the blue continuous line represents the ECD spectrum after flipping the sample (*back* side), *i.e.* with the deposition facing the detector; the black dashed line is the semi-sum of the two ECD spectra.

We prepared thin film samples of **1** by drop casting, *i.e.* depositing on a quartz plate about 100 μL of a 10^{-2} M solution of **1** in CHCl_3 , followed by slow evaporation of the solvent in an atmosphere saturated with CHCl_3 vapours. The UV-Vis absorption spectrum of the thin film (**Figure 2a**) showed a profile roughly comparable to the one observed in solution: the main bands fell between 350 nm and 500 nm, with a maximum at around 444 nm; furthermore, at long wavelengths a pronounced baseline drift was observed, due to scattering phenomena, which are common in solid samples. Switching to the chiroptical characterization, we observed a totally different situation from the solution state: in fact, the ECD spectrum of the thin film (**Figure 2b**, red line) revealed a very complex profile, consisting in a pair of weak negative bands around 520 and 470 nm and three strong bands, with maximum intensity at 420 nm ($g = -7.6 \times 10^{-3}$), 351 nm ($g = 1.3 \times 10^{-2}$) and 299 nm ($g = 1.8 \times 10^{-2}$) respectively, together with a long-wavelength tail allied to sample scattering. The anisotropy g -factors are noticeably large. Consistent profiles were obtained by recording ECD spectra at different rotation angles θ of the sample around the optical axis (horizontal) (**Figure S2** in Supplementary Information). This suggested an almost negligible contribution of the third term in Equation 1, as expected from the fact that the sample was obtained by drop-casting and cannot display any preferential orientation.

On the contrary, by flipping the sample, *i.e.* by turning it by 180° with respect to the vertical axis, we observed an almost mirror image spectrum to the previous one (**Figure 2b**, blue line), with two negative bands centred at 299 nm ($g = -1.9 \times 10^{-2}$) and 351 nm ($g = -1.1 \times 10^{-2}$), and a positive band at 420 nm ($g = 7.7 \times 10^{-3}$). Therefore, the thin film of our BDT-based oligothiophene **1** represents a very rare example of isotropic sample, undergoing (almost) complete reversal of the ECD signals upon switching the face of the thin film directed toward the incident light. The phenomenon is fully reproducible and was replicated for 5 separate samples, obtaining in each case identical results, including identical shapes and signs of the apparent ECD spectrum, and identical inversion upon flipping (**Figure 3**).

As a further control experiment, we synthesized the enantiomeric compound (*R*)-3,7-dimethyl-1-octyl-functionalised BDT-based oligothiophene *ent-1* starting from unnatural (*R*)-(+)- β -citronellol, following the same pathway shown in **Scheme 2**. The thin film ECD spectrum of *ent-1* revealed the same phenomenon of ECD inversion by sample flipping, but with a mirror-image behaviour compared to **1** (**Figure S3**, Supporting Information): for the *front* side of sample, we observed two negative bands centred at 299 nm and 351 nm. In addition, thin films obtained by drop casting of a solution containing equimolar amounts of **1** and *ent-1* (*i.e.*, a

Figure 3. Dissymmetry g -factor values at 299 nm recorded for the front and the back side of 5 distinct freshly prepared thin films of compound **1**.

racemic mixture), led to very weak ECD signals (**Figure S5**). These findings demonstrate that **1** and *ent*-**1** behave exactly as expected for a couple of enantiomers, whatever the source of their ECD signals of thin films.

To understand these latter ones, we must consider the various terms in Equation 1. The true circular dichroism (CD_{true}) is independent of sample orientation, while the LDLB effect (second term in Equation 1), dominates the chiroptical response to such a large extent to produce the uncommon g -factors mentioned above.

Since we can discard a role for the third term in Equation 1, the chiroptical signal can be considered the sum of CD_{true} , independent of sample orientation, and LDLB, which inverts upon sample flipping. Thus, if we take the average (semi-sum) of the two ECD spectra of **1** for the sample “back” or “front” to the light source, we isolate the genuine ECD contribution, as depicted in **Figure 2b**. Once again, the semi-sum spectrum of *ent*-**1** (**Figure S3**) turns out to be the mirror image of the same spectrum of **1**.

Artifacts due to simple LD or LB are quite common in solid-state ECD spectra, when the sample presents a desirable or even an unwanted anisotropy, which occurs for example upon stretching the film.⁵⁶ On the contrary, the LDLB effect with the associated ECD inversion appears unusual: in fact, to the best of our knowledge, it was reported before for chiral nematics, crystalline samples and notably for an achiral polyvinyl alcohol (PVA) film dyed with the achiral azo-compound Congo Red and highly stretched in order to make it macroscopically anisotropic.⁴⁴ In such a case, the onset of a LDLB term cannot be regarded as surprising: the Congo red molecules are definitely oriented and they surely display very large LD, while the stretched PVA film itself will definitely be birefringent.

Our BDT-based oligothiophene **1** films, instead, were prepared by drop casting, without any other operation which may impart a preferential molecular orientation. Thus, we have negligible *total* $\langle LD \rangle$ and $\langle LB \rangle$, *i.e.* the macroscopic quantities

averaged over the whole film. This is demonstrated by the invariance of the CD signal with respect to sample rotation around the incident light direction (angle θ in Equation 1).

Because

$$\langle LD \rangle = \langle LB \rangle = 0 \quad (2)$$

the only way to consistently have

$$\langle LD \cdot LB' \rangle + \langle LD' \cdot LB \rangle \neq 0 \quad (3)$$

is to assume that:

- 1) there are ordered domains where both linear properties do not vanish;
- 2) in all or at least a majority of these domains, the product $LD \cdot LB'$ (or equivalently $LD' \cdot LB$) is of one sign, in order to prevent cancellation over the whole sample;
- 3) because the prime indicates a $+45^\circ$ between the axes where LD and LB are referred, from the point of view of incident light, then this property is a manifestation of (supra)molecular chirality.

The situation is pictorially represented in **Figure 4**.

The occurrence of locally anisotropic and linearly birefringent domains is made evident by observing a thin film by means of a microscope with crossed linear polarisers, as shown in **Figure 5**. We can immediately notice that strongly birefringent spheroidal microdomains (diameter $< 500 \mu\text{m}$) stand out on a black background (*i.e.* with no LB).

By assuming that at least the first-level aggregates feature some alignment between conjugated BDT moieties packed with each other, the LD term is directly related to the polarization of the corresponding transition. In fact, the sequence of signs observed in **Figure 2** (blue or red traces) is in accord with the fact that the transition above 400 nm (#1 in **Figure 1d**) has different polarization with respect to the two

Figure 4. Schematic representation of the properties of the term $LD \cdot LB'$ responsible for the sign inversion of the ECD spectrum shown in **Figure 2b**.

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Figure 5. Optical microscopy images of chiral BDT-based oligothiophene **1** thin film sample: micrograph with non-polarized light (left); micrograph under cross-polarized filters (right).

transitions below 400 nm (#3 and #4, in **Figure 1d**), as demonstrated by TDDFT calculations. Assuming that LB remains of the same sign over a wider region, this simple reasoning accounts for the opposite signs of the strong transitions at 430 nm on one side and 380/300 nm on the other.

In order to better explain the situation, we can resort to a pictorial comparison. Our chromophore is flat just like any letter written on a glass surface. However, some letter like “p” would read “q” if watched *through* the glass. Indeed “p” and “q” are related by a mirror plane in two dimensions and can be considered 2-D enantiomers. If we cast a handful of “p”s onto a surface, they will randomly fall face-up or face-down and we’d obtain a 2-D racemate, *i.e.* an equal mixture of “p” and “q” which reads equally when watched from the two sides of the glass. In order to consistently have an excess of “p” from one side (*viz.* of “q” from the other), the two faces of the letter must be different: in such a way, the chance of landing face-up or face-down would be different. We may say that the two faces, which in principle are enantiotopic, must become diastereotopic. This is only made possible by a chiral element, which in the present case is provided by the branched alkyl chains.

A further puzzling aspect comes from solvent annealing, a common procedure to obtain more homogeneous samples of thin films. If we let the samples stand for a few minutes (up to about 15') in a chamber saturated with vapours of a “good”

solvent (CHCl_3), we obtain the ECD spectra displayed in **Figure 6**, which are (almost) invariant upon sample rotation (see **Figure S7** in Supplementary Information) *and also upon flipping*. Again, this has been repeatedly observed on up to 5 separate samples. This invariance guarantees that the spectrum is now fully LDLB effect-free and must be regarded as a genuine ECD. The intensity of the ECD signals is apparently reduced compared to those found on the freshly prepared samples. This can be explained by a simple comparison: the two dashed lines of **Figure 2** and **Figure 6** match almost perfectly (positions, signs and also amplitudes of the bands). Thus, the average spectrum found by taking the semi-sum of the two orientations for the original film is identical to the “true ECD” observed for the solvent-annealed film. This means that, in spite of the strong ECD signals due to the LDLB term, we may confirm that the semi-sum spectrum is a real representation of a the genuine ECD.

This spectacular change in the ECD spectrum is associated with no significant changes in the UV-Vis absorption spectrum, compared to the non-annealed film (**Figure 6a**), although with a different morphology of the thin film: in fact, optical microscopy images (**Figure 7**) display a more homogeneous texture, as if the small domains had melted and smeared into weakly birefringent “palm leaves-like” domains, suggestive of a nematic texture, although it is devoid of any significant LDLB effect.

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Figure 6. UV-Vis absorption (a) and ECD (b) spectra of **1** as thin film after 10 minutes of annealing with CHCl_3 vapour. Panel (b) shows ECD spectra recorded for the front (red line) and the back side (blue line) of the thin film, together with their semi-sum (dashed line).

By further exposure to the solvent vapours, we expected that the same process would proceed further, but on the contrary after 60 minutes of annealing we found again a clear LDLB effect similar to that measured on the freshly prepared sample: once more we recorded almost mirror-image profiles by sample flipping, as shown in **Figure 8b**. Again, taking the semi-sum of the two spectra left a small residual signal

(dashed line of **Figure 8b**) which reproduces the dashed lines of **Figure 2b** and **6b**.

What is really remarkable is that the dichroic signal is much stronger and consequently we also record higher g -factors, approaching values as large as 0.05 (more precisely it is 4.8×10^{-2} at 351 nm). These value is extraordinarily large for a purely organic system.

Figure 7. Optical microscopy images of chiral BDT-based oligothiophene **1** thin film sample after 10 minutes of annealing with CHCl_3 vapour: micrograph with non-polarized light (left); micrograph under cross-polarized filters (right).

Figure 8. UV-Vis absorption (a) and ECD (b) spectra of **1** as thin film after 60 minutes of annealing with CHCl_3 vapour. Panel (b) shows ECD spectra recorded for the front (red line) and the back side (blue line) of the thin film, together with their semi-sum (dashed line).

Optical microscopy investigation (**Figure 9**) on the fully solvent-annealed film revealed a highly homogeneously birefringent structure, where no local structure can be recognized. No further significant changes in spectroscopic and morphological properties were observed with longer annealing times.

It is clear that in all cases investigated, there is a constant background of a genuine ECD signature. This cannot be a property of isolated molecules, because we had found before that in solution **1** displays vanishing ECD. It must be the result of a well-defined chiral supramolecular structure, featuring a

twisted stack with negative helicity of the long molecular axis, on account of the signs of the ECD spectrum (with reference to the dashed lines in **Figures 2b**, **6b** and **8b**).⁵⁷ This means that at least the first level of hierarchy, which normally dominates the appearance of the ECD spectrum of supramolecular aggregates,⁵⁸ seems to be preserved among all investigated films, and almost unaffected by annealing. Solvent annealing has instead a strong impact on the organization at the mesoscopic level, as detected by optical microscopy. This is a

Figure 9. Optical microscopy images of chiral BDT-based oligothiophene **1** thin film sample after 60 minutes of annealing with CHCl_3 vapour: micrograph with non-polarized light (left); micrograph under cross-polarized filters (right).

Figure 10. Schematic picture of the double chirality issue discussed in the text. In both cases, we deal with left-handed supramolecular stacks, but on the left the molecules are oriented “face up” and watched from above one would read a “p”, while on the right the molecules are “face down” and one would read a “q”. These two situations lead to the same “true” ECD, which depends only on the helicity of the molecular stack, but to oppositely signed LDLB terms.

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rather unique case, in which the apparent ECD signal does suggest the occurrence of a complex aggregation pathway, but a more accurate analysis reveals the presence of a major first-order supramolecular aggregate characterized by a specific ECD signature. It is remarkable that this occurs only in the films upon solvent exposure, while in solution the molecules remain completely solvated until they precipitate.

The final schematic picture that may fit all the phenomena discussed so far is shown in **Figure 10**, where we exploit the above mentioned similarity with “p”/“q” enantiomerism in 2-D. Upon drop-casting, the molecules adhere on quartz preferentially on one face, let’s say “p”, because of intrinsic molecular chirality. Thereupon, they pack on top of each other in a helical stack with negative twist, possibly forming in a chiral nematic phase. ECD signal results from the sum of true ECD (CD_{true}) and LDLB term (Equation 1). The former is invariant, the latter is inverted upon sample flipping (“p” transforms into “q”), **Figure 2b**. Short time exposure to the solvent detaches these helices from the surface, which leads to their random orientation: they remain left-handed helices, but the expose both “p” and “q” faces to the light which leads to cancellation of the LDLB effect (while CD_{true} is conserved), **Figure 6b**. Finally, a longer annealing lets the molecules find their most stable configuration on the surface re-establishing the predominance of “p” and restoring a large LDLB term, **Figure 8b**.

Conclusions

Our chiral benzodithiophene derivative **1** displays an uncommon feature which leads to a very strong dichroism, with values almost 0.1, which is extraordinary for small organic molecules and only arises thanks to a remarkable supramolecular order. The origin of these strong signals stems from a LDLB effect, and as a consequence it completely inverts upon changing the direction of illumination: if light comes from the front or from the back of the sample, its chiroptical response will be opposite. This property, associated with the very strong *g*-value will be valuable for the conception of novel optoelectronic devices sensitive to the light source.⁵⁹⁻⁶⁰

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Table of contents

Chiroptical Response Inversion upon Sample Flipping in Thin Films of a Chiral Benzo[1,2-*b*:4,5-*b'*]dithiophene-based Oligothiophene

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Our drop-casted films display linear dichroism-linear birefringence interference (LDLB effect) with strong CD signals, which are inverted upon sample flipping.