Helicity Control of π-Stacked Assemblies of Oligo(*para*-phenylene) Derivatives Using Photoresponsive Chiral Moieties at Terminal Sites

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Oligo(*para*-phenylene) (OPP) derivatives bearing photoresponsive chiral dithienylethene (DE*) terminal moieties that induce chirality in the OPP main chain are synthesized. In the assembled state, the photoisomerization of the chiral DE* terminal moieties prior to assembly, from the open to the closed form, leads to a change in the helicity of the π-stacked structures. The circular dichroism spectra of mixed solvent solutions and cast films of the OPP assemblies exhibit bisignate Cotton effects in the absorption region associated with the oligomer main chain: these features indicate the presence of helically π-stacked structures. Furthermore, the chiral transcription of racemic poly(bithiophenethiophene) (PBTT) by chiral OPP in the assembled state is demonstrated. The chirally transcribed PBTT shows a change in helicity upon the photoisomerization of the chiral DE* terminal moieties of OPP. To the best of our knowledge, this is the first report of helicity control of a helically π-stacked conjugated oligomer through the photoisomerization of a chiral photoresponsive moiety. Such assemblies could be attractive for use in optoelectronic devices and optical memory systems.

1. Introduction

Many researchers have brought about chirality control in π-conjugated systems and polymers by changing the nature of the environment without affecting their stereocenters.[1] These changes in chirality have been generated by varying parameters such as the temperature,[2] pH,[3] and salt concentration.[4] One facile way to change the handedness of helical polymers and π-conjugated systems is to incorporate a photoresponsive chiral moiety within their structures.

Photoresponsive compounds have been widely researched and, due to their fast switching abilities, ease of synthesis, and versatility, have been used in a variety of applications. Photoresponsive chiral moieties have been used to control the helical sense of racemic polyisocyanate upon the absorption of circularly polarized light.[5] Furthermore, introduction of photoresponsive moieties in π-conjugated systems have made possible the switching of optoelectronic properties of conducting polymers,[6] photoinduced aggregates,[7] supramolecular assemblies,[8] and photoresponsive organogelators.[9] They have been also used for the dynamic switching of linearly polarized luminescence[10] and circularly polarized luminescence[11] and in the development of molecular nanomachines,[12] phototunable chiral nematic LCs,[13] and phototunable photonic bandgap materials.[14]

Azobenzenes, sterically overcrowded stilbenes, spiropyrans, azulenes, and flugides are examples of well-studied photochromic molecules that show reversible changes in their molecular structure and absorption spectrum upon photo- and/or thermal induction.[15] Chiral compounds having an azobenzene moiety have been used as chiral dopants due to their photochemical *trans–cis* isomerization behavior.[16] Although easy to synthesize, the azo group has low fatigue resistance and is thermally unstable.

Meanwhile, dithienylethene (DE) derivatives, which are also able to undergo structural changes between the open and closed forms via photoisomerization, are resistant to fatigue and are thermally stable. Therefore, it is advantageous to employ these derivatives as photochromic materials compared to other photoresponsive compounds.[15b,17]

Herein, we report the synthesis of oligo(*para*-phenylene) (OPP) derivatives that have photoresponsive chiral DE* terminal moieties. These terminal moieties induced chirality in the OPP main chains. We demonstrated that the photoisomerization of the chiral DE* terminal moieties from the open to the closed form, prior to assembly, leads to a change in the helicity of the formed π-stacked structures. Furthermore, the chiral transcription of racemic poly(bithiophenethiophene) (PBTT) by chiral OPP in the assembled state was also demonstrated. The chirally transcribed PBTT showed a change in helicity upon the photoisomerization of the chiral DE* terminal moieties of OPP. To the best of our knowledge, this is the first report of helicity control of a helically π-stacked conjugated oligomer through the photoisomerization of a chiral photoresponsive moiety. Such assemblies could be attractive for use in optoelectronic devices and optical memory systems.

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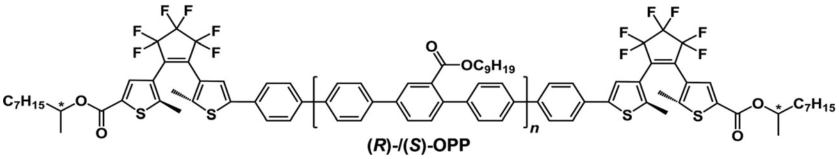


Scheme 1. Structure of the chiral OPP derivatives bearing photoresponsive chiral DE* terminal moieties.

2. Results and Discussion

2.1. Synthesis and Characterization of the Oligo(*para*-phenylenes)

Oligo(*para*-phenylene) derivatives bearing photoresponsive chiral dithienylethene moieties at the terminal sites were synthesized (**Scheme 1**). The OPP main chain was substituted with a *n*-nonyloxycarbonyl moiety, and the photoresponsive chiral DE* terminal moieties were substituted with a chiral nonyloxycarbonyl moiety possessing either (*R*)- or (*S*)- handedness ((***R***)**-** or (***S***)**-OPP**, respectively).

The experimental details and synthetic routes to the precursors, photoresponsive chiral DE* terminal moieties, monomers, and oligomers are shown in Scheme S1 in the Supporting Information. Briefly, the monomers *n*-nonyl-2,5-dibromobenzoate and 4,4'-biphenyldiboronic acid bis(trimethylene glycol) cyclic ester and the (***R***)**-/**(***S***)**-Br-DE*** terminal moieties were copolymerized via a Suzuki coupling reaction in which tetrakis(triphenylphosphine) palladium(0) (Pd(TPP)$_4$) was used as the catalyst. The reaction was conducted at 80 °C under an argon atmosphere using tetrahydrofuran (THF) and water as the solvent system. The reaction proceeded for 24 h, and then the oligomer was washed in water under constant stirring for an additional 24 h. Next, the precipitated oligomers were filtered and subsequently washed in methanol (MeOH) for 24 h. Finally, they were dried under vacuum.

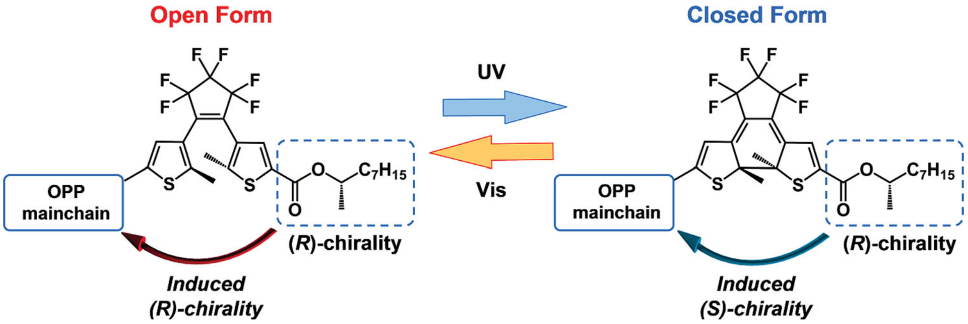
The number average molecular weight (M_n) and the polydispersity (M_w/M_n) of the oligomers were measured using gel permeation chromatography (GPC) (calibrated using a polystyrene (PS) standard). According to the GPC results, the M_n of the oligomers ranged from 4200 to 4600 and had M_w/M_n values of 1.1 and degrees of polymerization between 10 and 11 (Table S1).

2.2. Photoswitching Behavior of the Oligo(*para*-phenylenes)

The chirality of the synthesized OPPs bearing photoswitchable chiral DE* terminal moieties could be switched using UV and visible light. In the case of (***R***)**-OPP** bearing photoswitchable DE* with (***R***)-chirality, the chirality of the main chain could be controlled by changing the structure of the chiral DE* terminal moieties. Upon irradiation with UV light, the terminal moieties adopted a closed structure, which induced (***S***)-chirality in the OPP main chain in assembled state. Conversely, upon irradiation with visible light, the DE terminal moieties adopted an open structure, which induced (***R***)-chirality in the OPP main chain upon helical assembly (**Scheme 2**).

The photoisomerization of the chiral DE* terminal moieties of (***R***)**-/**(***S***)**-OPP** was examined via ^{1}H NMR (in $CDCl_3$) (Figure S1). Two broad signals were observed at 1.95 and 2.00 ppm, and these peaks were assigned to the methyl protons at the 5,5′ substitution position of the dithienylethene moiety in its open form. When the system was irradiated with UV light ($\lambda = 302$ nm, 16 W), photoisomerization occurred and two new broad signals at 2.21 and 2.25 ppm appeared, which corresponded to the methyl protons at the 5,5′ substitution position of the dithienylethene moiety in its closed form. The integrated intensities of the proton signals indicated that 98% of the open forms were converted to the closed forms in the photostationary states (PSS) of (***R***)**-OPP** and (***S***)**-OPP**. The PSS is defined as {[closed form]/([open form] + [closed form])} × 100.[15a,c] After subsequent irradiation of the systems with visible light ($\lambda > 400$ nm, 100 W), the only signals observed were those of the open form. The values of conversion of the PSS of the chiral DE* terminal moiety precursors, (***R***)**-/**(***S***)**-Br-DE*** were 84% and 83%, respectively (Table S2). The difference in conversion rate between (***R***)**-/**(***S***)**-OPP** and (***R***)**-/**(***S***)**-Br-DE*** could be related to the oligomer main chain of (***R***)**-/**(***S***)**-OPP** stabilizing the antiparallel conformation of the dithienylethene moiety.[18] Note that because the closed form is not completely formed after irradiation with UV light, we will refer to the mixture of structures obtained as the closed form/PSS from here on out.

The UV–vis absorption and circular dichroism (CD) spectra of the chiral DE* terminal moiety precursors, (***R***)**-/**(***S***)**-Br-DE***, in chloroform ($CHCl_3$) solution do not show absorption peaks in the visible range which is indicative of the open form of the compound (**Figure** 1a). Upon irradiation of (***R***)**-/**(***S***)**-Br-DE*** with UV light, the closed form/PSS exhibits absorption peaks and monosignate Cotton effects around 550 nm (Figure 1b). These bands originate from the extended conjugation between the thiophene rings and the six-membered ring that bridges



Scheme 2. Photoisomerization of the chiral DE* terminal moieties leads to a switching of chirality of the OPP main chain upon helical assembly.

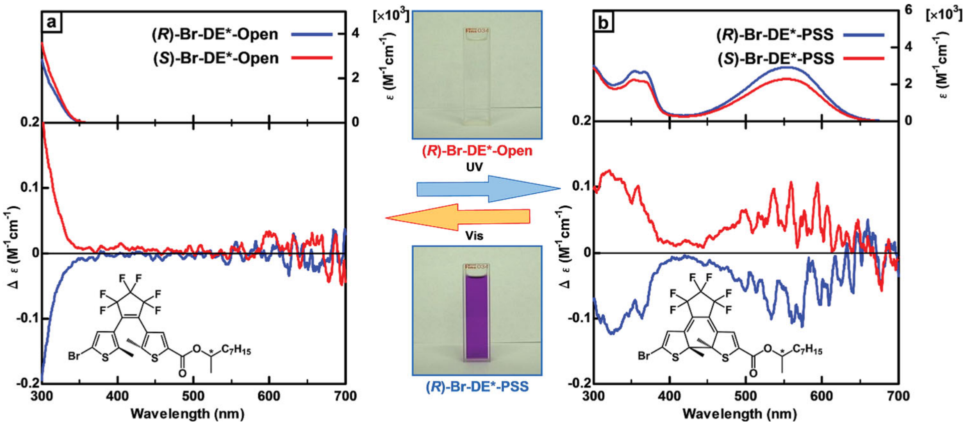


Figure 1. UV–vis (upper) and CD (lower) spectra of **(*R*)/(*S*)-Br-DE*** ($CHCl_3$ solution) in (a) open form and (b) PSS. Photograph of **(*R*)-Br-DE*** solution in open form (center top) and PSS (center bottom).

them in the closed form of the molecule. The **(*R*)-Br-DE*** solution shows photochromic behavior when the structure of the photoresponsive chiral terminal moiety changes.

Furthermore, a $CHCl_3$ solution of **(*R*)-OPP** shows photochromic behavior upon irradiation with UV light due to the emergence of an absorption peak at 600 nm, which is indicative that the chiral DE* terminal moieties are in the closed form (Figure S2). When the chiral DE* terminal moieties are in the open form, the UV–vis spectrum reveals an absorption peak at 340 nm from the OPP main chain. When the terminal moieties are in the closed form, a shoulder band emerges between 360 nm and 420 nm and the absorption peak of the terminal moieties are also present at 600 nm. The extended π-conjugation between the closed form of the chiral DE* terminal moieties and the OPP main chain leads to a bathochromic shift of the peak from 550 nm to 600 nm.

Measurements to determine the timescale of photoswitching between open form to PSS were performed (Figure S3). For **(*R*)-OPP** in $CHCl_3$ solution, we observed the emergence of the terminal moiety absorption band (600 nm) in less than 5s exposure of UV light. We observed a plateauing of the 600 nm band at 20 s of UV exposure corresponding to the PSS (Figure S3a). Upon exposure to visible light, the oligomer solution showed a complete switching to open form after 2 min (Figure S3b). Fatigue measurements were performed under cycles of UV and visible light exposure (Figure S3c). A gradual decrease of absorbance at 600 nm, correlating to the closed form/PSS state, was observed indicating that the photoisomerization conversion rate gradually decreases upon exposure to a number of UV and visible light cycles.[19]

It has been reported that the CD spectra of $CHCl_3$ solutions of aromatic conjugated polymers substituted with chiral nonyloxycarbonyl moieties, such as poly(thiophene) or poly(phenylthiophene), exhibit monosignate Cotton effects. These effects are due to the transfer of chirality from the chiral side chains to the main chain via “through bond interactions”.[20] In contrast, the CD spectra of $CHCl_3$ solutions of **(*R*)-/(*S*)-OPP** in both the open and closed forms did not exhibit Cotton effects. These results suggest that the OPP main chain does not form an intrachain one-handed helical structure in

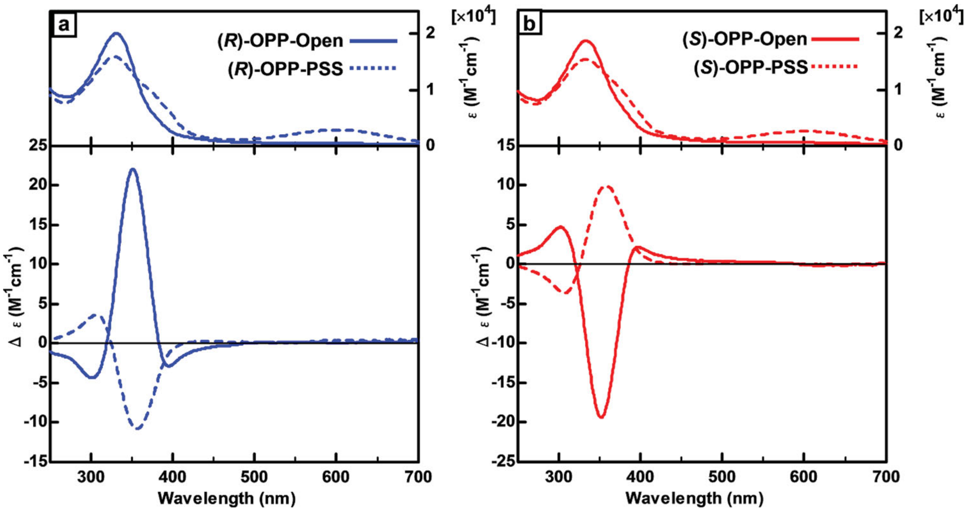


Figure 2. UV–vis (upper) and CD (lower) spectra of (a) **(*R*)-OPP** and (b) **(*S*)-OPP** in assembled state ($CHCl_3$:MeOH, 1:1 v/v solution) in open form and PSS.

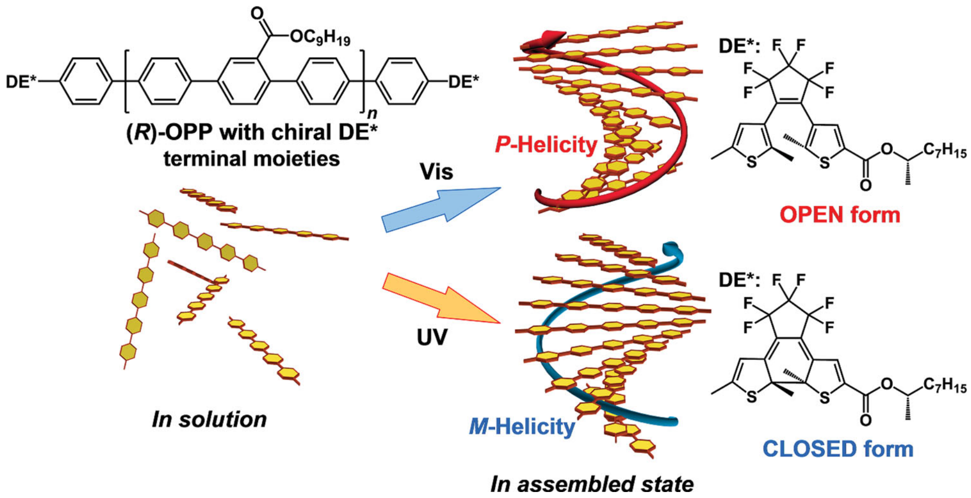


Figure 3. Schematic model of the helically π-stacked assemblies of **(*R*)-OPP** exhibiting opposite helical sense upon photoisomerization of the chiral DE* terminal moieties prior to assembly.

solution, likely because the chiral centre is located at the terminal sites, far from the OPP main chain. This distance makes intrachain chiral induction difficult.

2.3. Helical Switching of the OPPs in the Assembled State

In solution, **(*R*)-/(*S*)-OPP** do not exhibit Cotton effects. However, in the assembled state, the oligomers may exhibit helically π-stacked structures. For instance, highly planar thiophene-based aromatic conjugated copolymers, such as poly(diphenylenethiophene), have been reported to adopt helically π-stacked structures in the assembled state.[20] Thus, we investigated whether OPP could form helically π-stacked structures in the assembled state (either in a mixed solvent or a cast film system).

First, **(*R*)-/(*S*)-OPP** was dissolved in $CHCl_3$ and exposed to either UV (~20 s) or visible light (~2 min) to obtain the open or closed form of the chiral DE* terminal moieties. Then, a poor solvent (i.e., methanol (MeOH)) was added to the solution ($CHCl_3$:MeOH, 1:1 v/v) and oligomer assemblies were formed. The absorption and CD spectra of the oligomer assemblies were measured.

The CD spectra of **(*R*)-/(*S*)-OPP** revealed bisignate Cotton effects in the region associated with the OPP main chain, which suggests that helically π-stacked structures are formed in the assembled state (**Figure 2**). Upon photoisomerization of the chiral DE* terminal moieties prior to assembly, the chirality of the **(*R*)-/(*S*)-OPP** π-stacked assemblies are determined. Exciton coupling theory[21] indicates that the open form of **(*R*)-OPP** has *P*-helicity and a right-handed helically π-stacked structure, while the closed form/PSS of **(*R*)-OPP** has *M*-helicity and a left-handed helically π-stacked structure (Figure 2a). Assemblies of **(*S*)-OPP** showed opposite chirality at the open (*M*-helicity) and closed form (*P*-helicity) of the chiral DE* terminal moieties with opposite handedness relative to **(*R*)-OPP** (Figure 2b).

It should be noted that the Cotton effects of the open and closed forms of the **(*R*)-/(*S*)-OPP** assemblies were not

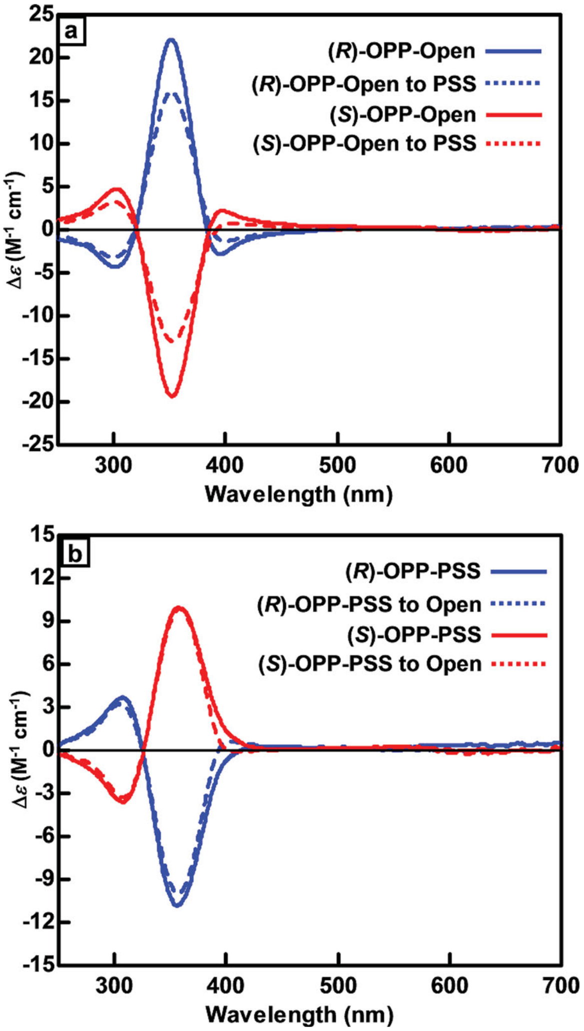


Figure 4. CD spectra of **(*R*)-(*S*)-OPP** in assembled state: (a) in open form, followed by exposure to UV light (transition: open form to PSS); (b) in PSS, followed by exposure to visible light (transition: PSS to open form).

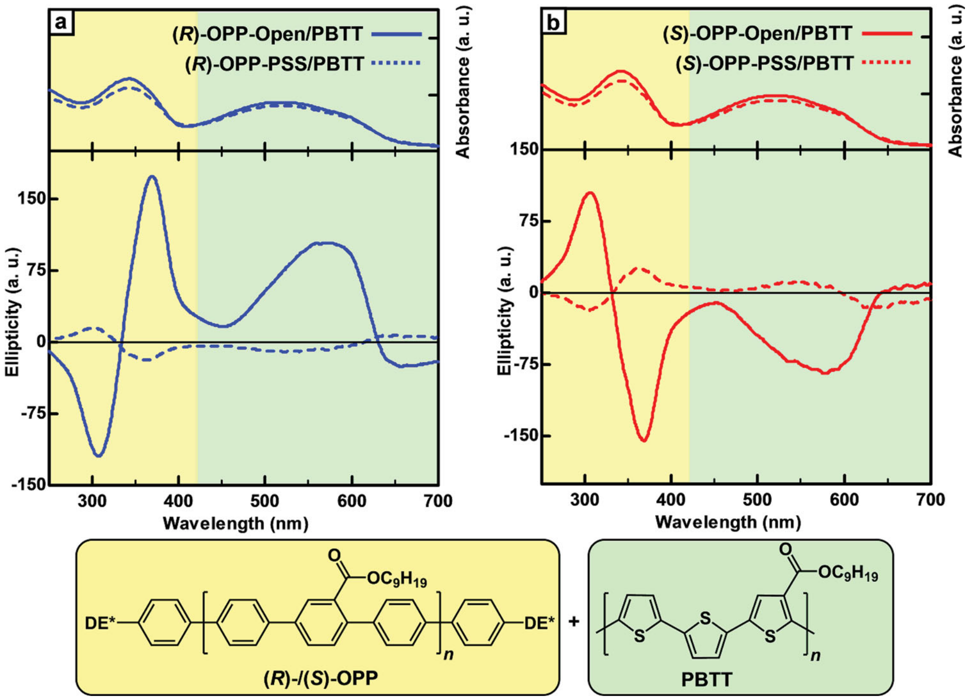


Figure 5. UV–vis (upper) and CD (lower) spectra of (a) **(*R*)-OPP/PBTT** cast film, and (b) **(*S*)-OPP/PBTT** cast film in open form and PSS. Shaded regions represent absorption regions of OPP (yellow) and PBTT (green).

symmetric, as the open form showed a larger intensity compared to the closed form. These results are related to the degree of conversion of the terminal moieties from the open to the closed form. Photoresponsive DE molecules show varying degrees of conversion from the open to closed form depending on their molecular structures as well as conditions including temperature and solvent environment.[17,22] In other words, when **(*R*)-/(*S*)-OPP** in its open form is exposed to UV light and photoisomerization occurs, not all of the chiral DE* terminal moieties are converted to the closed form. A difference in the chiral induction strength was observed for the open and closed forms of the chiral DE* terminal moieties in OPP because not all of the terminal moieties are converted. Furthermore, the open form of the chiral DE* end-group has a more bulky structure, which induces a more twisted helically π-stacked structure. These steric effects lead to a larger CD intensity. **Figure 3** shows a schematic model of the formation of helical π-stacked assemblies of **(*R*)-OPP** having either left- or right-handed helical sense in open form or closed form/PSS, respectively.

After the formation of the **(*R*)-/(*S*)-OPP** assemblies in the mixed solvent, subsequent photoisomerization of the chiral DE* terminal moieties from either the PSS to the open form or vice versa did not cause a significant change in the CD spectra of system (**Figure** 4). Such behavior was also observed with **(*R*)-OPP** cast films (Figure S4). During the formation of the oligomer assemblies, the handedness of the helically π-stacked structures was determined by the chirality of the DE* terminal moieties. In the assembled state, strong interchain interactions maintain the handedness of the helically π-stacked structures in spite of the photoisomerization of the chiral DE* terminal moieties.

2.4. Helical Switching of Achiral PBTT in the Assembled State through Chiral Transcription

We observed that **(*R*)-/(*S*)-OPP** form helically π-stacked structures in the assembled state in both mixed solvent solutions and cast films. Furthermore, we investigated the potential for the induction of chirality in a racemic polymer by chiral OPP through chiral transcription. First, **(*R*)-/(*S*)-OPP** was dissolved in $CHCl_3$ and was either exposed to UV or visible light to select the open or closed form of the chiral DE* terminal moieties. Then, a racemic polymer, poly(bithiophenethiophene) (**PBTT**), was added to the solution at a 1:1 mole ratio. The oligomer/polymer mixture was then drop-cast onto a quartz substrate, and the CD spectra of the resulting film was measured.

The CD spectrum of the **(*R*)-OPP-Open/PBTT** cast film shows bisignate Cotton effects from 250 nm to 400 nm and from 450 nm to 700 nm that are associated with the absorption of the main chain of OPP and PBTT, respectively (**Figure** 5a). The **(*R*)-OPP-PSS/PBTT** cast film shows bisignate Cotton effects associated with the OPP and PBTT absorption bands having opposite handedness relative to **(*R*)-OPP-Open/PBTT**. Likewise, **(*S*)-OPP-Open/PBTT** and **(*S*)-OPP-PSS/PBTT** show bisignate Cotton effects having opposite handedness relative to their **(*R*)-OPP/PBTT** counterparts (Figure 5b). The CD results suggest that chiral transcription occurred in racemic PBTT through the formation of interchain helically π-stacked structures consisting of chiral OPP and racemic PBTT.

Similar to **(*R*)-/(*S*)-OPP** system, the CD spectra of the **(*R*)-/(*S*)-OPP-Open/PBTT** system show larger intensities compared to those of **(*R*)-/(*S*)-OPP-PSS/PBTT**. These differences are also related to the degree of conversion of the DE moieties and the stronger chiral induction of the open form of the chiral DE* terminal moieties.

3. Conclusion

Novel photoresponsive OPP derivatives have been synthesized by introducing chiral, photoisomerizable DE* terminal moieties to the OPP main chain. In the assembled state, helicity control of the π-stacked structures was made possible upon the photoisomerization of the chiral DE* terminal moieties prior to assembly. Furthermore, we reported the chiral transcription of racemic PBTT through the formation of helically π-stacked assemblies consisting of photoresponsive chiral OPP and racemic PBTT. We show, for the first time, the helicity control of a conjugated oligomer through the photoisomerization of its chiral terminal moieties. These helicity-controllable photoresponsive OPP assemblies can potentially be used in the development of dynamic optical memory systems and functional chiroptical devices.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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[18] The dithienylethene molecule has two conformations with the two thiophene rings in mirror symmetry (parallel conformation) and in C_2 symmetry (antiparallel conformation). The photoisomerization can only proceed from the antiparallel conformation. In general, the population ratio of the two conformations is 1:1. However, incorporating the dithienylethene molecule into an oligomer chain stabilizes the antiparallel conformation. Thus we observe higher conversion rates from open to closed form in **(*R*)-/(*S*)-OPP** than the terminal moiety precursor (*R*)-/(*S*)-Br-DE*.

[19] Upon successive photoisomerization cycles, some of the open form dithienylethene moieties in parallel conformation are not photoisomerized back to the closed form. Fatigue resistance of the dithienylethene molecule can be improved with the introduction of bulky substituents to the thiophene rings preventing the parallel conformation at the open form. Design improvements of the chiral DE* terminal moieties to improve fatigue resistance will be carried out in future works.

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