Impact and Amplification of Chirality in the Aggregation of Leucine-Appended Poly(*p*-phenylene ethynylene) (PPE)

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Abstract

A leucine-appended poly(*p*-phenyleneethynylene) (PPE) was prepared in enantiomeric stereoregular (L-**1** and D-**1**) and stereorandom (rac-**1**) forms. The solution aggregates of L-**1**, D-**1**, rac-**1**, and mixtures of L-**1**/D-**1**, were characterized by absorption, electronic circular dichroism and emission spectra. Both rac-**1** and L-**1**/D-**1** mixtures are more prone to aggregate than L-**1** and D-**1**. Upon aggregating, the enantiomeric mixtures manifest an apparent majority-rules effect, which is mostly due to the greater tendency to form heterochiral aggregates with respect to homochiral ones. The impact of chirality on the aggregation behaviour of the aminoacid-appended PPE is demonstrated.

Keywords: conjugated polymers; chiral polymers; electronic circular dichroism; fluorescence quenching; supramolecular structure

Introduction

Conjugated polymers have been established as efficient and convenient starting materials for optoelectronic devices of various kinds, including sensors, transistors, solar cells and light-emitting devices.[1, 2] Despite the tremendous interest in the field, the fundamental properties responsible for successful optoelectronic applications, such as charge transport and exciton diffusion, remain to be fully understood.[3, 4] The reasons for this difficulty are manifold: the intrinsic structural complexity of the starting materials; the natural disorder of polymeric compounds and their aggregated states, especially thin films; the various and different levels of hierarchy of structural organization, from the molecular scale up to the mesoscale, which make it necessary to use different techniques for a full characterization.[5, 6] In turn, the degree of order reached at the various levels of hierarchy has an obvious impact on the device performance.[7-9]

We are especially interested in the design and characterization of chiral materials suitable for optoelectronic applications.[10-17] Chirality may play a decisive role in the emergent properties of materials for technological applications,[18] a role which has been often underestimated.[19] The presence of stereodefinite chirality elements in organic materials has several relevant consequences. Often, a stable supramolecular structure of π-conjugated polymers displays a parallel arrangement.[7, 20, 21] This corresponds to the most efficient packing and ensures charge mobility by hopping processes.[22] However, it also limits exciton lifetime and for this reason it may be considered undesirable.[23] Bulky groups prevent this parallel stack and introduce a twist between neighbouring groups.[24] In the lack of stereo-control, this twist is randomly distributed, causing disorder. On the contrary, specific stereo-controlled supramolecular architectures may be pursued, featuring a twisted arrangement with preferential helicity between immediate neighbours.[20, 23, 25, 26] The consequence of the different packing of racemic vs. enantiopure organic semiconductors on charge mobility has been very recently addressed and demonstrated.[18] To improve polymer processability, the introduction of branched chains is widespread, one above all being the 2-ethylhexyl moiety.[27] Such branched chains are inherently chiral and once chirality is introduced in the polymer, one may decide to leave it to its casual fate (i.e., using racemic or non stereodefinite chiral moieties) or to take full control of it (i.e., using stereodefinite chiral moieties).[12, 19] This latter option has the further bonus of opening the way to the use of chiroptical spectroscopies to study chiral supramolecular systems.[28-30] In particular, electronic circular dichroism (ECD) lends itself as an ideal tool for the characterization of conjugated polymers, providing information about the first level of supramolecular organization at the nm scale

which is hardly reached by microscopy. Finally, chirality is essential to develop optoelectronic devices based on circularly polarized light.[31, 32]

There is a fundamental question which arises whenever one deals with aggregates of chiral species: how does the presence, nature and incidence of chirality elements impact on the aggregation phenomena and on the supramolecular structures? This question – which also relates to the phenomenon of amplification of chirality – has been frequently addressed for supramolecular species obtained by discrete molecules (for example discoids and similar ones) or at most conjugated oligomers,[33] but much less so in the context of chiral conjugated polymers. This is rather surprising because any practical application of conjugated polymers relies on their aggregated states. ECD (together with other chiroptical methods) can be applied very proficiently to characterize solid-state aggregates occurring in thin films,[34] or alternatively, ECD can be used to monitor the aggregation in solution.[24, 35] Chiral polythiophenes (PT) are the most studied family of chiral conjugated polymers.[25, 26] In particular, several reports deal with the expression of supramolecular chirality in polymers constructed by monomers of varying enantiomeric excess,[36, 37] and block copolymers made up of chiral and achiral blocks in varying amounts.[38-40] Apart from these and a few other examples,[41] the role played by chirality in the aggregation properties of conjugated polymers has been largely overlooked. For example, poly[2-methoxy-5(2′-ethylhexoxy)-*p*-phenylenevinylene] (MEH-PPV) is a popular polymer for optoelectronic applications, and it is chiral; nonetheless, it has always been employed in its racemic or stereorandom form, although this latter manifests a different aggregation behaviour with respect to the enantiopure stereoregular form.[12] Another important family of conjugated polymers is that of poly(*p*-phenyleneethynylene)s (PPEs). They have found many useful applications, especially as sensors.[42-45] Several chiral PPEs have been reported by us[10, 11, 13, 46] and others.[47-53] However, in no case was the specific impact of chirality considered; interestingly enough, some oligo(*p*-phenyleneethynylene)s are known to show chirality amplification phenomena.[54-56]

Here, we describe the consequences of chirality on the aggregation behaviour of a PPE appended with side-chains derived from leucine methyl ester (**1**, Chart 1). Three different stereoisomers of **1** were prepared: the two stereoregular forms obtained from enantiopure L- and D-leucine (L-**1** and D-**1**, respectively), and the stereorandom form obtained from racemic DL-leucine (rac-**1**). Although the synthesis and characterization of L-**1** has been already reported before,[13] the answer to the aforementioned fundamental question about the impact of chirality on the aggregation phenomena may be answered only by considering the same polymer in the stereorandom form, and as mixture of the two stereoregular antipodes. In fact, the various forms of

the same polymer with different chiral composition (enantiopure polymers, their mixtures, and racemic polymer) must be regarded as distinct chemical entities when aggregation comes into play, yielding to different material properties.[18, 19] Here, we report a spectroscopic study on solutions and solution aggregates of rac-**1** and of blends of L-**1** and D-**1**, in comparison to those of pure L-**1** or D-**1**. Not only the stereorandom polymer displays a different tendency to aggregation than the stereoregular forms, but the analysis of blends of L-**1** and D-**1** at varying enantiomeric composition revealed a chirality amplification of the "majority-rules" type which is unprecedented for PPEs. The present study focuses on solution aggregates of polymer **1**; a full optical and chiroptical characterization of thin-film spectra is reported elsewhere.[15]

Results and discussion

Characterization of L-1, D-1 and rac-1: solution aggregates

The synthesis of L-**1**, D-**1** and rac-**1** was accomplished using the already reported procedure, based on the Cassar-Heck-Sonogashira polymerization methodology.[13] The experimental details and the synthetic scheme are reported in the Supporting Information. The new polymers D-**1** and rac-**1** were prepared respectively from D-leucine and DL-leucine methyl ester. Note that rac-**1** was obtained by polymerizing the racemic monomer in a stereorandom way; the co-polymerization between L-leucine and D-leucine monomers was not performed. The resulting polymers were characterized in the same way described for L-**1**,[13] and showed consistent average properties (see Supporting Information for details): M_n = 5.5-6.2 kDa (GPC), polydispersity index PDI = 1.3-1.4 (GPC), diffusion coefficient 2.2-2.4×10^{-10} m^2 s^{-1} (DOSY-NMR, in CDCl$_3$, 25°C). Such data indicate an average length of about 16 phenylene units. Short polymers (or oligomers) are ideal to observe a higher degree of chirality transfer from chiral side-chains to supramolecular aggregates.[12]

UV-vis absorption, ECD and fluorescence spectra were measured in dichloromethane and in dichloromethane/diethyl ether mixtures (Figure 1). Because the polymers are soluble in chlorinated solvents, molecularly dispersed non-aggregated species can be observed in CH$_2$Cl$_2$ solutions. Conversely, the polymers are insoluble in Et$_2$O. Therefore, CH$_2$Cl$_2$/Et$_2$O solutions represent the typical conditions encountered for mixtures of a "good" solvent with a "poor" solvent (or non-solvent), which progressively promote aggregation in solution upon increasing the fraction of the "poor" solvent (in this case Et$_2$O). Absorption and ECD spectra of L-**1** and D-**1** are reported in Figures 1a and 1d. In CH$_2$Cl$_2$, the absorption spectra show a broad band with maximum centred at 432 nm, associated with the major $\pi-\pi^*$ transition of the conjugated alkoxy-substituted PPE

backbone.[43, 44] The corresponding ECD spectra are negligible, with g-factors ($\Delta\varepsilon/\varepsilon$ or $\Delta A/A$) around 10^{-5} (Figures 1b and e). Although L-**1** and D-**1** are both chiral and chromophoric, the chiral groups are far from the chromophoric backbone and exert only a small chiral perturbation on the chromophore transitions.[13, 30] Addition of the "poor" solvent causes a clear solvatochromism in the absorption spectra: the main band is red-shifted and becomes narrower, and a so-called aggregation band appears at 490−495 nm which increases upon promoting the aggregation (ESI, Figure S1).[24, 43, 44, 57-61]

Both changes are allied with two concomitant phenomena, namely aggregation in solution, accompanied by the rigidification and planarization of the PPE backbone.[44, 62, 63] The sharp and red-shifted aggregation band is a typical manifestation of J-type aggregation[64] of rod-like *para*-PPE, which yields extensive aggregates in three directions, promoted by π-stacking between the aromatic backbones and ancillary interactions between the side-chains (dispersive forces between alkyl chains or, in the current case, hydrogen bonding).[65, 66] In contrast, chiral *meta*-PPE and discoid-like oligo(*para*-phenyleneethynylene)s (attached to 1,3,5-trisubstituted benzene core) prefer to adopt a coiled supramolecular structure whose spectral features may be described as H-type aggregates.[67-69]

The occurrence of aggregation of L-**1** and D-**1** is definitely proved by the evolution of ECD spectra.[24, 47, 51, 58] Upon addition of Et$_2$O, a structured ECD signal appears which may be described as an asymmetric exciton couplet with vibronic sub-bands (Figure 1b,e).[11, 70] The ECD spectra recorded for L-**1** and D-**1** in the same conditions are mirror images of each other; the ECD couplet is positive for L-**1** and negative for D-**1**. The most intense ECD band is observed at 490−495 nm, in correspondence with the aggregation band in the absorption spectra. The corresponding g-factors attain a value of about 4×10^{-3} already in the presence of 50% Et$_2$O, and remain almost constant upon further aggregation (see ESI, Figure S2). The ECD profile, the mirror-image relationship for the two samples, and the intensity of the ECD signals (in particular the 400-fold increase in the g-factor) call for the formation of an ordered supramolecular species, held together by π-stacking between the aromatic backbone and hydrogen bonding between side-chains, with a well-defined helicity between polymer chains packed on the top of each other.[11, 13, 30] The supramolecular helicity is right-handed for L-**1** and left-handed for D-**1**. The presence of an isodichroic point, the evolution of the absorption and ECD profiles, and the similar values of g-factors observed for samples dissolved in 50-70% Et$_2$O, demonstrate the presence of a single or largely preferential aggregate species in solution, with no hint of multiple aggregation pathways,[71] at least in the present conditions.[15]

The results discussed so far reproduce the behaviour previously observed for a different batch of L-**1**.[13] On the other hand, the mirror-image relationship observed for the aggregate ECD spectra of L-**1** and D-**1** was not reported previously, and it is a crucial piece of information to confirm the genuine nature of such ECD spectra. More significant results were observed by characterizing the stereorandom polymer rac-**1**. The UV-vis absorption spectrum measured for rac-**1** in CH_2Cl_2 is practically indistinguishable from that of the enantiopure samples L-**1** and D-**1**; however, it displays a different solvatochromic behaviour (Figure 1g). The onset of the aggregation band occurs for a smaller fraction of the "poor" solvent Et_2O (a small shoulder is visible already for 40% Et_2O), and for rac-**1** the band is stronger and more pronounced than for L-**1** and D-**1** for all corresponding solvent mixtures (ESI, Figure S1). Overall, the stereorandom polymer features a more pronounced tendency to aggregation in solution than the stereoregular analogues. The same behaviour was found before for the above mentioned MEH-PPV,[12] while, at best of our knowledge, no similar observation has been reported to date for chiral PPEs. Of course, ECD spectra of the stereorandom polymer rac-**1** were silent for all solvent mixtures (Figure 1h).

The fluorescence emission spectra of the three samples in CH_2Cl_2 and CH_2Cl_2/Et_2O solvent mixtures (Figure 1c, f and i) are in keeping with the known behaviour of PPEs and further support the conclusions drawn from absorption and ECD spectra. In CH_2Cl_2 solutions, the polymers L-**1**, D-**1** and rac-**1** manifest the typical broad emission band with maximum at about 476-478 nm with a long-wavelength (probably vibronic) shoulder. The observed Stokes shift with respect to the main absorption band is around 35 nm, a common value for dialkoxy-substituted PPEs.[43] The addition of the "poor" solvent – triggering the aggregation – causes hypo/hypsochromism of the main emission band, which can be assigned to the molecularly dissolved polymer. Concomitantly, a new band appears at 504-505 nm which can be assigned to the aggregated species.[43] The aggregate is much less emissive than the non-aggregated polymer, because its emission originates from low-energy traps reached after exciton migration;[23] therefore, the aggregation causes a progressive quenching of the overall photoemission, a very well-known phenomenon for PPEs.[43] It is however noteworthy that the aggregates of **1** remain a little emissive even in the presence of the largest amount of Et_2O (80%) and give rise to a further broad band above 525 nm which can be assigned to excimer-like species.[43, 72] Additionally, it is also interesting that the emission quenching is more pronounced for the stereorandom polymer rac-**1** than for the stereoregular ones L-**1** and D-**1**. The integral ratio between the residual emission in 20/80 CH_2Cl_2/Et_2O solution and the original emission in CH_2Cl_2 is 12% for rac-**1** and 17% for D-**1** and L-**1**, respectively. The difference is small but reproducible, and appears more evident by plotting the emission intensity as a function of the Et_2O fraction (see ESI, Figure S3). A similar difference in the quenching of

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fluorescence emission between stereoregular and stereorandom polymers was already observed before for MEH-PPV,[12] but it is unprecedented for PPEs. Its importance lies in the fact that the survival of even a small emission efficiency in PPE aggregates is mandatory for optoelectronic applications, and it is one of the main reasons for designing chiral PPEs.[25, 26] In fact, the presence of stereoregular elements of chirality favours a twisted supramolecular arrangement between polymer chains with respect to a less emissive parallel alignment.[23, 24]

Characterization of L-1/D-1 blends: chirality amplification

The above discussed results demonstrated a first effect of chirality on the aggregation behaviour of the leucine-appended PPE **1**: the stereorandom rac-**1** has more pronounced tendency to aggregate than the enantiopure form. It appears relevant to understand if heterochiral pairing is preferred to homochiral pairing, that is, if aggregates are preferentially formed from polymeric chains of the same configuration (homochiral) or of different configuration (heterochiral). To this end, we analysed the blends of the two stereoregular polymers L-**1** and D-**1**. Such blends were prepared by mixing different ratios of the two polymers in CH_2Cl_2/Et_2O solvent mixtures. The 40/60 CH_2Cl_2/Et_2O mixture was chosen as the best condition to observe solution aggregates, because it was the mixture richest in poor solvent which afforded the strongest ECD signal stable for a long time, i.e., without the occurrence of detectable precipitation. Two stock solutions of L-**1** and D-**1** in CH_2Cl_2 were separately prepared and their exact concentration estimated by absorption spectra. Then, adequate amounts of the two solutions were mixed and diluted with CH_2Cl_2 and Et_2O, yielding nine samples with enantiomeric excesses (e.e.) ranging from 100% pure D-**1** to 100% pure L-**1**. Their UV-vis absorption and ECD spectra are shown in Figures 2 and 3. The absorption spectra immediately reveal that the blends of L-**1** and D-**1** aggregate more favourably than the separated polymers; this means that heterochiral interactions are favoured over homochiral ones. Interestingly enough, the addition of a small amount of L-**1** to D-**1** (or vice-versa) promotes a more extensive aggregation, as demonstrated by the evolution of the aggregation band at 490−495 nm (notice that all spectra in Figure 2 were measured on samples with the same total polymer concentration).

Moreover, the stereorandom polymer rac-**1** also behaves differently from the racemic mixture of L-**1** and D-**1**, this latter being again more prone to aggregate (see comparison in the ESI, Figure S5). In the same conditions of poor solvent fraction, in fact, the aggregation band is more pronounced for the racemic mixture than for the stereorandom form.

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Since the absorption spectra evidenced the occurrence of favourable heterochiral interactions, it was not a surprise to observe that the ECD spectra of the blends manifested a non-linear relationship with the enantiomeric excess. The ECD spectra preserved the same shape and profile along the series (Figure 3a). However, a plot of the ECD intensity at 495 nm (corresponding to the first and strongest ECD band) led to the trend depicted in Figure 3b. The ECD intensity varies non-linearly with the e.e. (the ideal linear relationship is indicated by the dashed line in the graph), which is again a direct evidence of heterochiral interactions.[33] Moreover, the positive deviation from linearity confirms that such heterochiral interactions are indeed favourable. The chirality amplification effect observed for **1** recalls what is called "majority-rules" principle: it occurs in covalent polymers or in supramolecular aggregates of chiral monomers when the excess of one enantiomer leads to a bias toward the supramolecular helicity preferred by that enantiomer.[33, 73, 74] Majority-rules effects have also been observed for the supramolecular aggregates of some chiral polymers,[36, 75] but they are unprecedented for PPEs. In fact, to the best of our knowledge, chirality amplification effects have never been reported before for poly(*p*-phenyleneethynylene)s, although they were observed for short oligo(*p*-phenyleneethynylene)s with 3 or 4 phenyleneethynylene units.[54-56, 67]

In the present case, the apparent amplification of the chiroptical response shown in Figure 3b is mainly related to a larger degree of aggregation found for heterochiral aggregates with respect to homochiral ones, rather than to a true majority-rules phenomenon. In fact, the intensity of the aggregation band (495 nm) in the absorption spectra of the L-**1**/D-**1** blends also displays a pronounced deviation from linearity as a function of the enantiomeric excess (see ESI, Figure S4). As a consequence, by plotting the *g*-factor at 495 nm rather than the ECD intensity (Figure 3c), an almost linear trend is recovered, showing only a small positive deviation from linearity. It must be stressed that the present experiments are based on the formation of a supramolecular aggregate which is not under thermodynamic control. However, since all described samples (with variable solvent composition or enantiomeric ratio) were prepared independently, the dispersion of data in the trends shown in Figures 3 and S1-S4 (ESI) offers a direct estimation of the reproducibility of experiments and the validity of our results. As far as the *g*-values are concerned, we may estimate a maximum error of 10-15% (see Figure S3). Therefore, the non-linear effect reported in Figure 3c can be considered genuine though minimal. In fact, the trend follows a symmetric sigmoidal shape centred at 0% e.e. and almost all points feature a consistent deviation from linearity rather than a scattered one. Even admitting a 15% error on the *g*-values, the sigmoidal trend would be preserved.

The above discussed behaviour is pictorially illustrated in Figure 4. In Et$_2$O-rich solvent mixtures, L-Leu-C6-PPE (L-**1**) forms homochiral aggregates with preferential right-handed helicity. Upon adding a small quantity of the opposite enantiomer D-Leu-C6-PPE (D-**1**), the aggregation is further pushed on, by forming preferentially heterochiral aggregates over homochiral ones. In fact, the absorption aggregation band becomes more pronounced and the ECD increases in intensity, yielding for the overall ECD signal a large positive deviation from linearity. These heterochiral stacks preserve the same helicity and shape of the homochiral ones, as witnessed by the similar ECD profiles. This increased aggregate formation is the major responsible for the enhanced chiroptical response, possibly accompanied by a small majority-rules effect, as demonstrated by the small positive deviation from linearity shown by the *g*-factor dependence on the enantiomeric excess.

Conclusions

We studied the impact of stereochemistry on the aggregation of Leu-C6-PPE (**1**) in solution by comparing the behaviour of two enantiomeric stereoregular polymers synthesized by L-Leu and D-Leu, their blends with various enantiomeric excesses, and the stereorandom polymer synthesized by DL-Leu. In each case, aggregation in solution was promoted by the use of solvent mixtures composed of a "good" solvent (CH$_2$Cl$_2$) and a "poor" solvent (Et$_2$O). The solution aggregates were characterized by absorption, ECD and emission spectra.

Three different phenomena were discovered which depend directly on the presence, nature and incidence of chirality in the aminoacidic sidechains. First, the stereorandom polymer (rac-**1**) is more prone to aggregate than the stereoregular polymers (L-**1** and D-**1**). Second, enantiomeric mixtures of L-**1** and D-**1** are also more prone to aggregate than their components. Third, these enantiomeric mixtures manifest a pronounced amplification of chirality, which is mostly due to the stronger tendency to aggregate, and to a small extent is related to a majority-rules effect.

The three phenomena confirm that chirality plays indeed a major role in the aggregation behaviour of aminoacid-appended poly(*p*-phenyleneethynylene)s, and more in general of conjugated polymers. This characteristic may be exploited in the design of new materials for optoelectronic applications.

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Figure Captions

Chart 1. Structure of the polymers investigated (Leu-C_6-PPE **1**).

Figure 1. Absorption (a, d, g), ECD (b, e, h), and fluorescence (c, f, i) spectra of L-Leu-C6-PPE (L-**1**, blue hue, top row), D-Leu-C6-PPE (D-**1**, red hue, middle row), and DL-Leu-C6-PPE (rac-**1**, green hue, bottom row) in CH_2Cl_2/Et_2O mixtures with increasing amounts of Et_2O. Samples concentration 0.024 mg/mL; cell length 1 cm; excitation wavelength 435 nm.

Figure 2. Absorption spectra of blends of L-Leu-C6-PPE (L-**1**) and D-Leu-C6-PPE (D-**1**) with variable enantiomeric composition, in 40/60 CH_2Cl_2/Et_2O solvent mixtures. Samples concentration 0.024 mg/mL; cell length 1 cm.

Figure 3. (a) ECD spectra of blends of L-Leu-C6-PPE (L-**1**) and D-Leu-C6-PPE (D-**1**) with variable enantiomeric composition, in 40/60 CH_2Cl_2/Et_2O solvent mixtures; same conditions as in Figure 2. (b,c) Plots of the ECD intensity and *g*-factor at 495 nm as a function of the enantiomeric excess. The fitting curves are polynomials; the dashed and dotted lines show the ideal linear trends.

Figure 4. Pictorial representation of the aggregation process of L-**1** (yielding a homochiral aggregate), which is further favoured in the presence of a small amount of D-**1** (yielding a heterochiral aggregate).
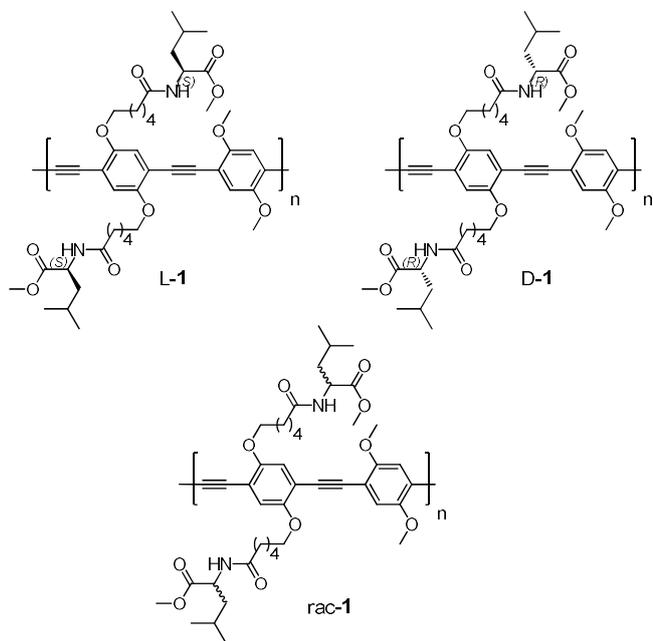
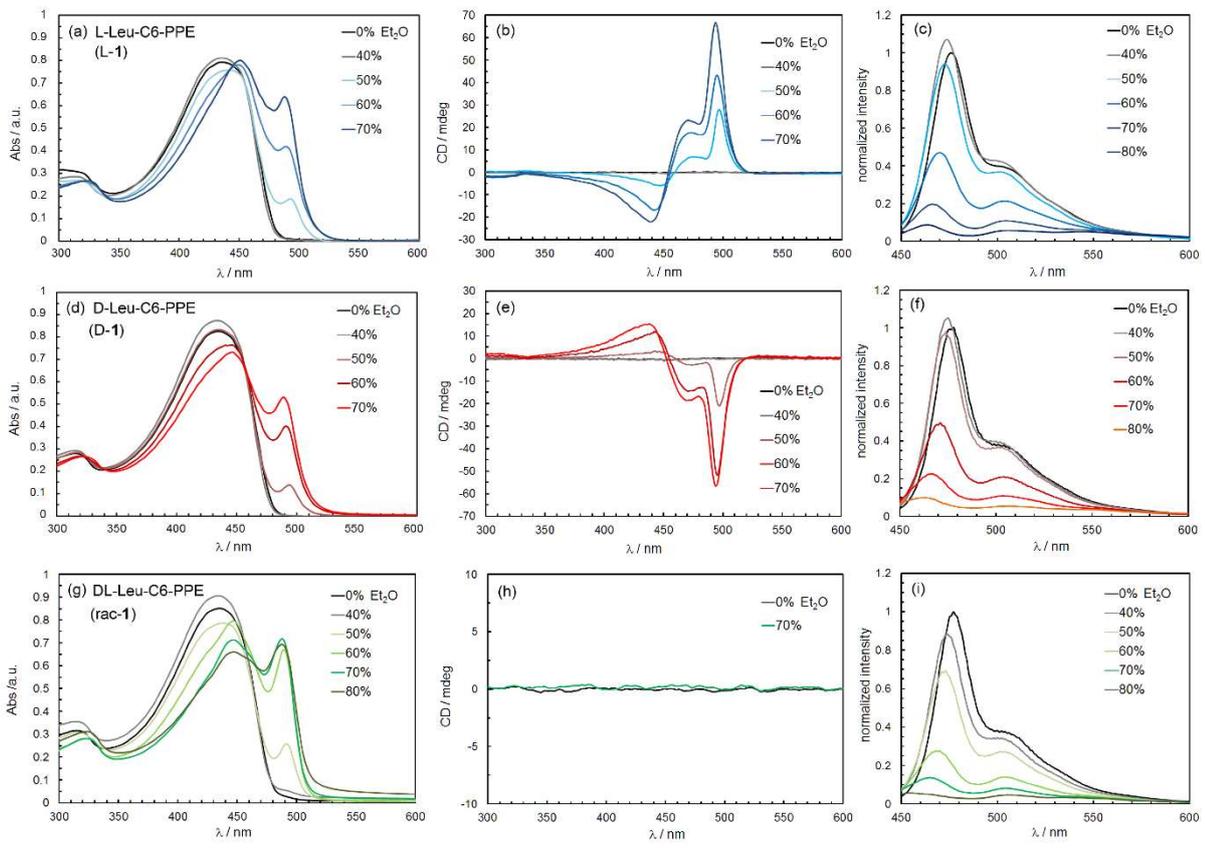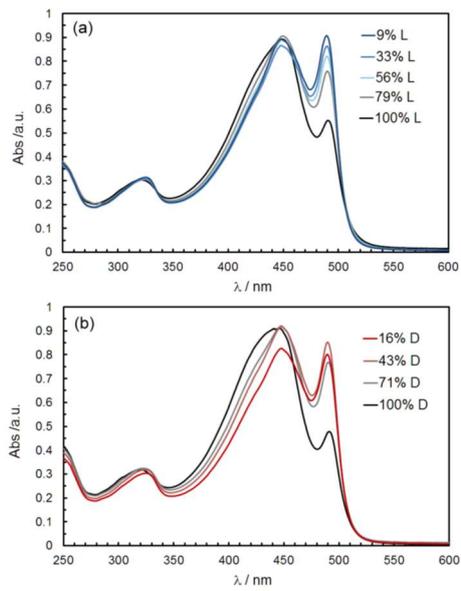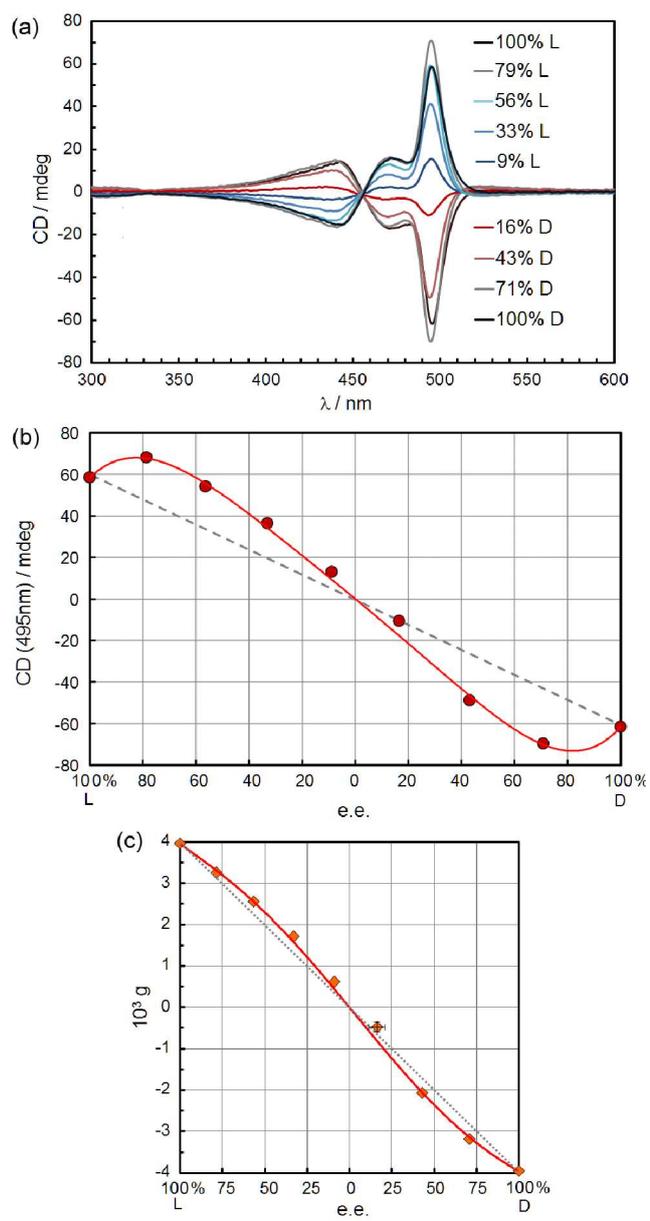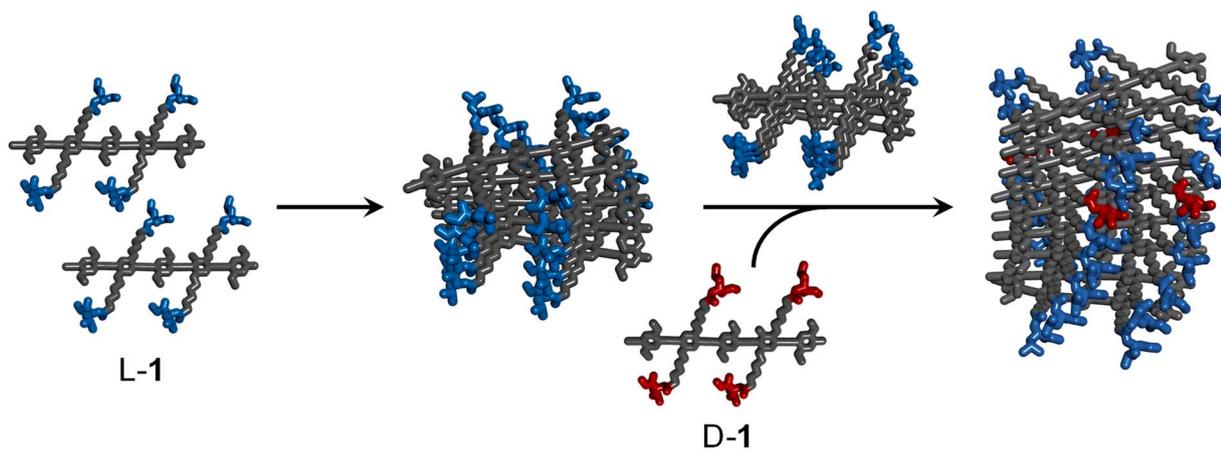**CHARTS and FIGURES**

Chart 1

Figure 1

Figure 2

Figure 3

Figure 4

Graphical Abstract