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Limone Induced Chirooptical Generation and Inversion during Aggregation of Achiral Polyfluorene Analogs: Structure-dependency and Mechanism

Laibing Wang, a Nozomu Suzuki, b Jiangfei Liu, a Takashi Matsuda, b Nor Azura Abdul Rahim, b Wei Zhang, * a Michiya Fujiki, * a Zhengbiao Zhang, a Nianchen Zhou a and Xiulin Zhu a

Chirality transfer from biological agents to π-conjugated polymers in solid state is an attractive method to generate, switch, and amplify chirality, especially when one considers several potent device applications. However, the polymer-structure dependence on the solvent-induced chirality transfer mechanism is not well understood. To elucidate the structural-chiroptical property relationship of the polymer aggregates, poly(9,9-di-octyfluorenyl-2,7-diyl) (PF8), poly(9,9-di-octylsilica-fluorenyl-2,7-diyl) (PSi8), poly-(1-octylnonyl)-9H-carbazole-2,7-diyl) (PCz8), P(F8-alt-Si8), P(F8-alt-Cz8), and P(Si8-alt-Cz8) were synthesized. The limone chirality was efficiently transferred to PF8, PSi8 and P(F8-alt-PSi8) aggregates in CHCl3/limonene/CH3OH terosolvent, but the optical activity was not observable for PCZ8, P(F8-alt-PCZ8), and P(Si8-alt-PCZ8). The reason for the absence of chiroptical activity in Cz8-containing polymers could be that those polymers have stronger polarity compared to limonenes, and thus the interaction between limonene and polymer chain was too weak compared to interaction among Cz8-containing polymers. Surprisingly, chiroptical inversion in CD spectra between PF8 and PSi8 aggregates was found. More surprisingly, chiroptical inversion between CD and CPL spectra of PSi8 aggregates was observed. The unique chiroptical inversion was attributable to the opposite Mulliken charges between 9-Si in Si8 and 9-C in F8 unit and between Cipso(1) in Si8 and Cipso(1) in F8 unit. Another possible reason for this unexpected chiroptical inversion behaviour is the opposite direction of dipole moments presented in three stable rotational isomers of equatorial limonene rotamer.

Introduction

Solvent chirality transfer to racemic, and/or achiral molecules and polymers allows us to instantly generate optically active substances without any specific catalysis at ambient temperature. 1 So far, successful works on chirality transfer have been reported for aromatic ketones, 2a aliphatic ketones, 2b aliphatic carbonyl compounds, 2c rare earth (Eu 3+ and Tb 3+) complexes with organic ligands, 2d,2e π-conjugated oligomers 2f–a, polycyclic compounds, 2l,2m syndiotactic polystyrene in film state by solvent vapor and thermal annealing, 2k and azobenzene derivatives. 2n

Recently, optically active π- and σ-conjugated polymers have received much attention due to their elaborate chiroptical applications including circular polarization related photonic devices. However, it is often more expensive or time consuming to attach chiral side chains to the polymers or to synthesize a chiral catalyst that enables efficient chiral polymerization. Therefore, molecular chirality transfer using inexpensive, non-toxic chemicals that are commercially available is very attractive in terms of green and cost-effective chiral materials synthesis. Thus far, solvent chirality transfer to the aggregates of achiral or racemic polymers has been achieved in polysilanes 3a,3b dialkylpolyfluorenes, 3c–3h hyperbranched dialkylpolyfluorene 3i,3l and diarylpolyacetylenes 3i,3l

In some cases, aggregation plays a key role in chirality transfer because the above polymers dissolved in pure chiral solvents in the absence of poor solvent do not exhibit any detectable circular dichroism (CD) and circularly polarized luminescence (CPL) signals. Furthermore, when the aggregation process is involved, several π- and σ-conjugated molecules, oligomers, and polymers show significant enhancement in (ch)optical properties in the ground and excited states. Several aggregation induced (ch)optical transition behaviors are classified as aggregation induced emission (AIE), 4 aggregation-induced emission enhancement (AIEE), 5 aggregation-induced circular dichroism (AICD), and aggregation-induced CPL (AICPL). 3,5 As an example of AICD, solvent quantity of chiral solvents such as limonene, α-pinene, and alcohols facilitates to induce optical activity to several achiral polymers including polysilanes 3b, polyfluorene analogs 3d,3i and oligophenyles 2g in aggregate states. Note that
these chiral solvents are inexpensive, naturally occurring resources and the resulting aggregates can be formed in a minute. Though a choice of chiral solvent and a tuning of volume fractions of poor solvents and chiral solvents are known to be the critical factors for efficient chirality transfer to the aggregates of π-conjugated polymers, the role of the polymer chemical structure in the aggregate state is not fully understood.

To elucidate how the polymer backbone structure affects the limonene chirality transfer to the aggregates of π-conjugated polymers, we employed a series of π-conjugated polymers, poly(9,9-di-n-octylfluorenyl-2,7-diyli) (PF8), poly(9,9-di-n-octylsila-fluorenyl-2,7-diyli) (PSi8), poly(9-(1-octylnonyl)-9H-carbazole-2,7-diyli) (PCz8), P(F8-alt-Si8), P(8,8-octylfluorenyl-2,7-diyli) (PCz8) and P(Si8-alt-Cz8) (Scheme 1), as the model polymers. Herein, we found (i) chirality transfer as AICD and AICPL for PF8, PSi8, and their copolymers involving P(F8-alt-Si8) and P(F8,8-octylfluorenyl-2,7-diyli)20, (ii) non-detectable optical activity for Cz8-containing polymers, including PCz8, P(F8-alt-Cz8), and P(Si8-alt-Cz8), and (iii) CD chiriptical inversion between PF8 and PSi8 in aggregate states. In this work, we propose a mechanism to explain the difference between (i) and (ii). The existence of relatively strong dipole moments in Cz8 derivatives enables polymers to strongly interact each other and does not allow limonene molecules to be stacked between π-conjugated rings. In the case of (iii), the difference in electronattractivity between Si and C could be responsible for altering the pattern of intermolecular interaction between limonene and polymers. Another possible reason for (iii) is the opposite direction of dipole moments presented in three stable rotational isomers of equatorial limonene rotamer. The present experimental and theoretical works will present how subtle differences in polymer chemical structures in the ground and excited states dramatically change generating and switching chiroptical properties, which leads to rationally designing chirality transfer experiments in aggregate states of the polymers.

Scheme 1. Chemical structures of poly(9,9-di-n-octylfluorenyl-2,7-diyli) (PF8), poly(9,9-di-n-octylsila-fluorenyl-2,7-diyli) (PSi8), poly(9-(1-octylnonyl)-9H-carbazole-2,7-diyli) (PCz8), P(F8-alt-Si8), P(8,8-octylfluorenyl-2,7-diyli)20, P(F8-alt-Cz8), P(Si8-alt-Cz8), (R)-limonene (1R) and (S)-limonene (1S).

Results and Discussion

Spectroscopy (UV-vis, CD, PL, and CPL).

UV-vis and PL Analysis. The details of synthesis and characterization of polymers (GPC curves in Fig. S1) shown in Scheme 1 are given in supplementary information. Fig. S2 shows the UV-vis and PL spectra, which are achiral optical properties of a series of polymers in Scheme 1. The results show the optical properties of polymers in dispersed solution states (CHCl3) as well as in aggregation states (CHCl3/(1R)limonene (1R) or (S)-limonene (1S))/CH2OH. For UV-vis spectra in dispersed solution state, all polymers showed very similar absorption peaks around 300–450 nm. When the polymers aggregated in the mixed tersolvents system (CHCl3/(1R or 1S)/CH2OH), slight red-shifts (ranging from 3 nm to 27 nm) in UV-vis spectra were observed. For the PF8 aggregate, a new absorption peak appeared around 438 nm, which was not detectable for the other homo- and copolymers. This was attributed to the emergence of a chiral β-phase in the tersolvents.20 The common π–π absorption band near 400–410 nm and 350–360 nm is ascribed to the chiral α-phase. For the PL emission, the intensities of all the polymers in aggregation states were relatively weaker than those in CHCl3 solution, which is due to the aggregation-caused quenching (ACQ) mechanism.21

Polymer Structure Dependency of Chiroptical Properties. Our previous results demonstrated that the molecular weight of poly(9,9-di-n-decyfluorene) has obvious effect on the chiroptical properties.22 The current system is focused on the structure-dependency and mechanism of solvent-induced chiroptical properties of achiral polyfluorene analogs. Circular dichroism (CD) and circularly polarized luminescence (CPL) were employed to characterize the chiroptical properties in the ground and excited states, respectively. Figs. 1a and 1b present the typical CD and UV-vis spectra of homopolymers (PF8, PSi8 and PCz8) and alternating copolymers (P(F8-alt-Si8), P(F8-alt-Cz8), P(Si8-alt-Cz8)) in CHCl3/(1R or 1S)/CH2OH. Additionally, UV-vis and CD spectra of P(8,8-octylfluorenyl-2,7-diyli)20 are given in Figs. S2i, S2j, S4. All polymers did not show any Cotton CD signals in CHCl3/(1R or 1S)/CH2OH = 0.3/1.2/1.5 (v/v/v), which demonstrated the appearance of the aggregation of the polymers. The sizes of polymer aggregates are in the range of 410-1030 nm (Table S1).

Table 1 The assignment of CD sign and UV-vis excitation/absorption maxima (λmax) of seven polymer aggregates.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>CHCl3/1R/CH2OH system</th>
<th>CHCl3/1S/CH2OH system</th>
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<tbody>
<tr>
<td></td>
<td>λmax (nm)</td>
<td>λmax (nm)</td>
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<tr>
<td></td>
<td>sign</td>
<td>sign</td>
</tr>
<tr>
<td>PF8</td>
<td>(–)438</td>
<td>(–)357</td>
</tr>
<tr>
<td>PSi8</td>
<td>(+)406</td>
<td>(+)306</td>
</tr>
<tr>
<td>PCz8</td>
<td>(–)406</td>
<td>(–)306</td>
</tr>
<tr>
<td>P(F8-alt-Si8)</td>
<td>(–)438</td>
<td>(–)357</td>
</tr>
<tr>
<td>P(F8-alt-Cz8)</td>
<td>(–)438</td>
<td>(–)357</td>
</tr>
<tr>
<td>P(Si8-alt-Cz8)</td>
<td>(–)438</td>
<td>(–)357</td>
</tr>
<tr>
<td>P(F8,8-octylfluorenyl-2,7-diyli)20</td>
<td>(–)360</td>
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However, fluorescence optical microscope (FOM) images of polymer aggregates presented in Fig. S5, including three homopolymers (PF8, PSi8, PCz8) and one alternating copolymer P(F8-alt-Si8) with 1R and 1S, clearly showed larger dot like images that have typically 4-5 μm in diameter. These apparent larger images are attributable to the effect of optical blur on visualization. Contrarily, aggregates of P(Cz8-alt-Si8) and P(Cz8-alt-Cz8) with 1R and 1S did not clearly provide much dot like FOM images. PF8 aggregates in CHCl3/(1R/CH2OH showed three distinct CD extrema in the region of the π–π* transition (Fig. 1a), which potentially can be attributed to the chiral β-phase (negative sign at 438 nm) and the chiral α-phase (negative sign at 412 nm and positive sign at 357 nm), as reported earlier.23 In opposite handed chiral solution, CHCl3/(1S/CH2OH, PF8 showed the opposite CD signal at a
similar wavelength as the CHCl$_3$/1R/CH$_3$OH system. Both UV-vis and CD spectra confirmed the absence of $\beta$-phase in PSi8 aggregate. All results are summarized in Table 1.

![Graph](image)

**Fig. 1** Chiroptical properties of homo- and co-polymer aggregates. (a) UV-vis and CD spectra of PF8, PSi8 and their copolymers in tersolvents at 25 °C. Conditions: CHCl$_3$/1R or 1S/CH$_3$OH = 0.3/1.2/1.5 (v/v/v) for PF8 (1.94 × 10$^2$ mg mL$^{-1}$) and PSi8 (1.41 × 10$^2$ mg mL$^{-1}$), solvent fraction = 0.3/0.8/1.9 for P(F8-alt-Si8) (7.92 × 10$^3$ mg mL$^{-1}$). (b) UV-vis and CD spectra of C28-containing polymers in tersolvents at 25 °C. Conditions: solvent fraction = 0.3/1.2/1.5 for PC28 and 0.3/0.8/1.9 for P(C28-alt-F8) and P(C28-alt-Si8). (c) CPL and PL spectra excited at 360 nm of PF8, PSi8, and P(F8-alt-Si8) at 25 °C. Condition: fraction = 0.3/1.2/1.5 for PF8 and PSi8, and 0.3/0.8/1.9 for P(F8-alt-Si8). The concentrations of the polymers are the same as those in Fig. 1b except 1.98 × 10$^2$ mg mL$^{-1}$ for P(F8-alt-Si8).

To investigate which species in copolymers account for the CD signals, it is worth-noting the similarity in CD spectra. The shape of the CD spectrum of P(F8$_{80}$-ran-Si8$_{20}$) was similar to that of PF8, and CD intensity of P(F8$_{80}$-ran-Si8$_{20}$) was much weaker than that of PF8 (Figs. 1a and S4). On the other hand, the CD spectrum shape of P(F8-alt-C28) was similar to that of PSi8. These results indicate that in P(F8-alt-Si8) aggregate, there is a competition between F8 and Si8 to dominate CD spectra, and Si8 is relatively more dominant in the effect for CD spectra. The C28-containing homopolymer (P(C28)) and its alternating copolymers (P(F8-alt-C28) and P(Si8-alt-C28)), however, did not show any detectable CD signals in both aggregate and solution state with limonene (Figs. 1b, and S3). The possible reasons for element-dependent chiroptical inversion and CD inactive C28-containing polymers and aggregation mechanism will be discussed later (see below).

The structure change between ground state and excited state can be discussed by comparing the values of $g_{\text{CPL}}$ and $g_{\text{CD}}$. Fig. 1c shows the CPL and PL spectra (excited at 360 nm) of PF8, PSi8 and P(F8-alt-Si8) aggregates in the chiral tersolvents at 25 °C. The signs of CPL signals at 441 nm (1R) and 442 (1S) of PF8 are identical to the signs of CD at 438-nm (1R) and 436-nm (1S), which are the first Cotton π→π* CD bands. The magnitude of the $g_{\text{CPL}}$ value (-5.2 × 10$^3$ (1R)) is almost double of the corresponding gCD value (ca. -2.0 × 10$^3$ (1R)) from the 438-nm CD band. Similarly, the magnitude of the gCPL value (+1.5 × 10$^3$ (1S)) is slightly greater than that of the corresponding gCD values (ca. +1.1 × 10$^3$ (1S)) from the 438-nm CD band. If any significant structural change takes place in the ground and excited states, the gCPL value is expected to exhibit a different value, and in some cases, the sign inversion is possible. However, we evaluated that gCD = [Ellipticity (in mdeg)/32980]/Absorbance, while the absorbance is apparent value including an increase due to scattering effect. Thus larger value $g_{\text{CPL}}$ compared to $g_{\text{CD}}$ could arise from the scattering effect, so we cannot clearly say if there is large structural difference in ground and excited states.

Similarly, the agreement in the sign of $g_{\text{CPL}}$ and $g_{\text{CD}}$ at the first Cotton bands were confirmed P(F8-alt-Si8) aggregates. For P(F8-alt-Si8), gCD and gCPL values were +4.2 × 10$^3$ (423 nm) and +1.2 × 10$^3$ (426 nm) for the 1R system, and -3.9 × 10$^3$ (414 nm) and -0.4 × 10$^3$ (428 nm) for the 1S system. Note that, for P(F8-alt-Si8), the absolute magnitudes of the gCPL values are greatly increased by at least one third, compared to the corresponding gCD values regardless of limonene chirality. Possibly, this is arising from significant reorganization of inter and intra polymer chains within chiral aggregates in the excited state since the light scattering is expected to increase the relative value of gCPL but not to decrease it.

However, the disagreement in the sign of gCPL and gCD at the first Cotton bands was observed in PSi8 aggregates. The gCD and gCPL values were +4.2 × 10$^3$ (423 nm) and -0.4 × 10$^3$ (428 nm) for 1R system, and -3.9 × 10$^3$ (414 nm) and +1.2 × 10$^3$ (426 nm) for 1S system, respectively. This chiroptical inversion between the ground and excited states might reflect from significant reorganization including twisting direction of inter and intra polymer chains within chiral aggregates in the excited state, as discussed later (Table 2).

Because the choice of chiral/poor solvents and their volume fractions is one of the most critical factors for the aggregation behaviors, we tested (1) seven poor solvents and (2) nine different solvent fractions in the CHCl$_3$/1R or 1S/CH$_3$OH system in more detail. Firstly, among the seven poor solvents, the absolute CD and gCD values were maximized when most polar CH$_3$OH was employed for PF8, PSi8, and P(F8-alt-Si8) (see, Fig. S6). This indicates the fact that the interaction between limonene and polymer is maximized...
because these two compounds are categorized as non-polar groups and thus increase the chance of chirality transfer to the aggregates of π-conjugated polymers. Secondly, as expected, the relative volume fraction of methanol (poor solvent) and limonene (chiral source) clearly affected the absolute CD and gCD values (Fig. S7). Both an abundant amount of poor solvent and chiral source result in inefficient limonene chirality transfer to the aggregates of above π-conjugated polymers. This is because there is a competition in aggregate making and an abundance of chiral source to induce chirality, where poor solvent is responsible for the former and limonene is responsible for the latter. This optimization is crucial when applying this method to chirioptical device fabrications. Here again, the chirioptical inversion in the ground state between PF8 and PSi8 or P(F8-alt-Si8) was confirmed.

Nonlinear chirioptical amplification, well-known as the majority rule mechanism of (1) and (2) by focusing on (i) stability and optical activity difference in polymers depending on the dihedral angle of the main chain, and (ii) interaction among polymer and chiral source by analyzing Mulliken charges and dipole moments.

Potential Energy Surface of TriF1, TriSi1, and TriCz1. Because the twisting ability in the polymer backbone is the key to understanding the origin of optical activity, we calculated potential energy surfaces (PESs) of TriF1, TriSi1, and TriCz1 as models of the corresponding PF8, PSi8, and PCz8. Energy calculation was carried out in DFT B3LYP/6-31G(d,p) calculation. Fig. 2 (top) shows PESs as a function of dihedral angle (15° interval including 0°) between aromatic rings. To clarify why it favors twisted geometries, schematic drawing of aryl trimer and bipheryl is illustrated in Fig. 2 (bottom-left). Evidently, all TriF1, TriSi1, and TriCz1 cannot adopt coplanar trans (dihedral angle θ = 0°) and cis (θ = 180°) conformations in the ground states due to inherent H–H steric repulsive forces between aryl groups, as depicted in Fig. 2 (top). TriF1, TriSi1, and TriCz1 had global minima at θ = ±30° (anti-form) and local minima at θ = ±150° (syn-form). These inherent non-coplanar characteristics resemble the built-in nature of bipheryl to be twisted by θ = ±30° (Fig 2, bottom-right).

Plausible Mechanism of “Chiroptical Inversion” and “Chiral Aggregation” Mechanism.

In the previous section, we demonstrated (1) chirality transfer as AICD and AICPL for PF8, PSi8, and their copolymers, which did not occur for Cz8-containing polymers, and (2) CD chirioptical inversion between PF8 and PSi8 in aggregate states. For (2), it has been reported that chirioptical inversion in chiral oligomers/polymers,1e-g9 achiral polymers2h,10 polymers3,11,12 gel, and supramolecules13 are susceptible to physical and chemical stimuli. However, such an element-dependent chirioptical inversion is relatively rare. We discuss the
energy barrier heights imply that those chemicals are able to twist freely between left and right. The subtle differences in $E_b$s between TriF1, TriSI1, and TriCz1 are ascribed to the H–H distance between two aryls: 2.133 Å for TriF1 ($\theta = \pm 30^\circ$), 2.151 Å for TriSI1 ($\theta = \pm 30^\circ$), and 2.106 Å for TriCz1 ($\theta = \pm 30^\circ$). Shorter H–H distance should increase $E_b$ values between $\theta = \pm 30^\circ$. However, energy barrier heights between anti- and syn-forms are sufficiently high: TriF1 has $\approx 102$ kJ mol$^{-1}$, TriSI1 $\approx 90$ kJ mol$^{-1}$, and TriCz1 $\approx 57$ kJ mol$^{-1}$. This is probably due to a greater loss of $\pi$-electron delocalization energy at $\theta = \pm 90^\circ$.

All TriF1, TriSI1, and TriCz1, hence, PF8, PSi8, PCz8, P(F8-alt-Si8), P(F8-alt-Cz8), and P(Si8-alt-Cz8), disfavor adoption of coplanar trans and cis conformations in fluidic solutions, possibly, even in the aggregates. We did not see any significant difference in PESs among trimer models, which implies the twisting property accounts for neither chiroptical inversion nor chiral generation mechanism.

Simulated CD and UV spectra of TriF1, TriSI1, and TriCz1 at $\theta = 30^\circ$ (right handed) and 150° (left handed) obtained with TD-DFT calculation (B3LYP/6-31G(d,p) basis set) are depicted in Fig. 3. The UV $\Delta\epsilon_{\text{max}}$ and CD $\Delta\alpha_{\text{max}}$ values of TriSI1 are slightly longer by $\approx 5$ nm than those of TriF1 and TriCz1. However, the $\Delta\epsilon$ value at 350 nm of TriSI1 with dihedral angle of 30° is considerably weakened, compared to that of TriSI1 ($\theta = 150^\circ$), TriF1 ($\theta = 30^\circ/150^\circ$), and TriCz1 ($\theta = 30^\circ/150^\circ$). This weakening in CD amplitude of TriSI1 may be related to the marked reduction in $|\Delta\epsilon|$ values of PSi8 aggregates compared to that of PF8 and P(F8-alt-Si8) aggregates (Figs. S6-S8). However, it is worth noting that no significant difference in theoretical CD spectra among the twisted trimers can be seen. Hence, the origins of CD inversion between PF8 and PSi8 and of CD silence in PCz8 as aggregate forms cannot be explained by PES and calculated CD spectra.

![Fig. 3 Simulated CD and UV spectra (with full width at half maximum ($\text{fwhm}$) of 0.1 eV) of (a, b) TriF1, (c,d) TriSI1 and TriCz1 at dihedral angles of 30° and 150° obtained with TD-DFT calculation (B3LYP/6-31G(d,p) level).](image)

Mulliken charges and dipole moments of F8, SI8, and Cz8. To understand the interaction properties among polymer, chiral solvent, and poor solvent, Mulliken charges and dipole moments of F8, SI8 and Cz8 (Scheme 2) in ground and excited states were obtained with DFT and TDDFT calculations (B3LYP/6-31G(d,p) level) (Table 2, and Figs. S10 and S11). Interestingly, Cz8 has a large electric dipole moment of 2.15 Debye, while F8 and SI8 have weak dipole moments, 0.27 Debye and 0.30 Debye, in ground state, respectively. Thereby Cz8 has strong polarity, but F8 and SI8 are rather weak. It is possible that the intense polar nature of Cz8 rings prevents inducing optical activity because stacking interaction among Cz8s (interaction between polar and polar molecules) are stronger than the stacking of Cz8 and limonene (interaction between polar and non-polar molecules). According to a previous report, among various non-polar and polar chiral sources, less-polar limonene and α-pinene are capable of inducing optical activity in the polymer aggregates, but relatively polar (S)-/(R)-carvone, (S)-2-methyl-1-butanol, l-menthol did not induce any detectable CD active polymer aggregates.

Although the direction of the dipole moment in total is the same, it is notable that, for F8, Mulliken charges of 9-C and Cipso(1) have $-0.11$ and $+0.30$, whereas, for SI8, 9-Si and Cipso(1) are $+0.62$ and $-0.12$, which is opposite to the former. The switching in the charge between $9$-C/9-Si and Cipso(1)/Cipso(1) may be related to the CD inversion between PF8 and PSi8 aggregates. We assume that IR, with a slight polarity to one direction, interacts with PF8 and forms a right handed form which results in negative CD signal. If the polarity of the PSi8 is opposite to the PF8, it has the chance to form an opposite handed structure. The other factor involved in the chiroptical inversion could be the Mulliken charges and dipole moments of IR, which has three stable equatorial rotamers (Fig. S12, Tables S2 and S3 and related discussion).

As given in Table 2, for F8, Mulliken charges of 9-C in the ground and excited states have $-0.11$ and $+0.93$ that are opposite sign. Contrarily, for SI8, Mulliken charges of 9-Si in the ground and excited states have $+0.62$ and $+0.81$ that are same sign. The same sign of Mulliken charges at 9-Si in the ground and excited states may be related to the chiroptical inversion in the CD and CPL spectra of PSi8 aggregate.
Conclusions

We have demonstrated a novel element-dependent chiroptical inversion and structural dependence of π-conjugated polymers with the help of limonene chirality in aggregation states, which was confirmed with CD and/or CPL spectroscopy. Though chirality transfer was not observed in CHCl₃ (1R or 1S) cosolvent, in solution state. By inducing aggregation using the tersolvent system, CHCl₃ (1R or 1S)/CH₂OH, chirality was successfully transferred to PF₈ and PSi₈ or (PF₈-alt-Si₈) aggregates. The opposite CD signal between PF₈ and PSi₈ or (PF₈-alt-Si₈) were detected in (i) several poor solvents, (ii) various volume fractions of limonene and CH₂OH, (iii) different limonene enantiopurity, and (iv) different polymer concentrations. These results indicate that the chiroptical inversion is maintained well and not susceptible to those factors. The element-dependent chiroptical inversion was attributed to the opposite arrangement between polymer and limonene since the Mulliken charges of 9-Si in Si₈ and 9-C in F₈ units are opposite. The cause of CD inactive Cz₈-containing polymers in similar conditions could be ascribed to the strong polarity of the Cz₈ unit. Furthermore, whether Mulliken charge of 9-X (X= C and Si) in the ground and excited states is same or opposite may be related to the chiroptical inversion in the CD and CPL spectra of PF₈ and PSi₈ aggregate. Our work affords a better understanding of limonene chirality induced chiroptical generation, inversion, and retention of π-conjugated polymers in aggregation states, which provides a new approach to the design of functional assemblies with chirality.

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Notes and references


Graphical Abstract

Limonene Induced Chiroptical Generation and Inversion during Aggregation of Achiral Polyfluorene Analogs: Structure-dependency and Mechanism

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Herein, chiroptical inversion in CD spectra between PF8 and PSi8 aggregates was found. The unique chiroptical inversion was attributable to the opposite Mulliken charges between 9-Si in Si8 and 9-C in F8 and between Cipso(1) in Si8 and Cipso(1) in F8.
(R)-limonene

\[ \text{(R)-limonene} \]

(S)-limonene

\[ \text{(S)-limonene} \]