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## ARTICLE

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

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Chirality transfer from biological agents to  $\pi$ -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-*n*-octylfluorenyl-2,7-diyl) (**PF8**), poly(9,9-di-*n*-octylsila-fluorenyl-2,7-diyl) (**PSi8**), poly(9-(1-octylnonyl)-9*H*-carbazole-2,7-diyl) (**PCz8**), **P(F8-*alt*-Si8)**, **P(F8-*alt*-Cz8)**, and **P(Si8-*alt*-Cz8)** were synthesized. The limonene chirality was efficiently transferred to **PF8**, **PSi8** and **P(F8-*alt*-PSi8)** aggregates in CHCl<sub>3</sub>/limonene/CH<sub>3</sub>OH ternsolvent, 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 C<sub>ipso</sub>(1) in **Si8** and C<sub>ipso</sub>(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.<sup>1</sup> So far, successful works on chirality transfer have been reported for aromatic ketones,<sup>2a</sup> aliphatic ketones,<sup>2b</sup> aliphatic carbonyl compounds,<sup>2c</sup> rare earth (Eu<sup>3+</sup> and Tb<sup>3+</sup>) complexes with organic ligands,<sup>2d,2e</sup>  $\pi$ -conjugated oligomers<sup>2f-h</sup>, polyisocyanate,<sup>2i,2j</sup> syndiotactic polystyrene in film state by solvent vapor and thermal annealing,<sup>2k</sup> and azobenzene derivatives.<sup>2l</sup>

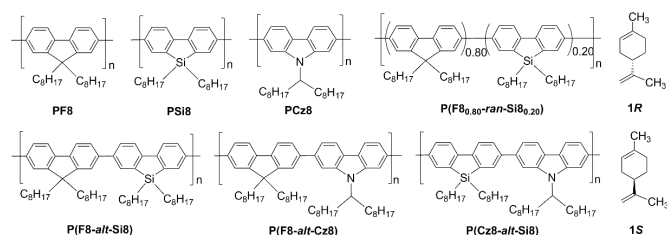
Recently, optically active  $\pi$ - and  $\sigma$ -conjugated polymers have received much attention due to their elaborate chiroptical applications including circular polarization related photonic devices. However, it is often more expensive or time consuming to attach chiral side chains to the polymers or to synthesize a chiral catalysis 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,<sup>3a,3b</sup> dialkylpolyfluorenes,<sup>3c-3h</sup> hyperbranched dialkylpolyfluorene<sup>3i,3j</sup> and diarylpolyacetylenes.<sup>3k,3l</sup>

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  $\pi$ - and  $\sigma$ -conjugated molecules, oligomers, and polymers show significant enhancement in (chir)optical properties in the ground and excited states. Several aggregation induced (chir)optical transition behaviors are classified as aggregation induced emission (AIE),<sup>4</sup> aggregation-induced emission enhancement (AIEE),<sup>5</sup> aggregation-induced circular dichroism (AICD), and aggregation-induced CPL (AICPL).<sup>3,6</sup> As an example of AICD, solvent quantity of chiral solvents such as limonene,  $\alpha$ -pinenes, and alcohols facilitates to induce optical activity to several achiral polymers including polysilanes,<sup>3b</sup> polyfluorene analogs<sup>3d,3j</sup> and oligophenylenes<sup>2g</sup> 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  $\pi$ -conjugated polymers,<sup>3</sup> 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  $\pi$ -conjugated polymers, we employed a series of  $\pi$ -conjugated polymers, poly(9,9-di-*n*-octylfluorenyl-2,7-diyl) (**PF8**), poly(9,9-di-*n*-octylsila-fluorenyl-2,7-diyl) (**PSi8**), poly(9-(1-octylnonyl)-9*H*-carbazole-2,7-diyl) (**PCz8**), **P(F8-*alt*-Si8)**, **P(F8<sub>0.80-ran</sub>-Si8<sub>0.20</sub>)**, **P(F8-*alt*-Cz8)** 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<sub>0.80-ran</sub>-Si8<sub>0.20</sub>)**, (ii) non-detectable optical activity for **Cz8**-containing polymers, including **PCz8**, **P(F8-*alt*-Cz8)**, and **P(Si8-*alt*-Cz8)**, and (iii) CD chiroptical 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  $\pi$ -conjugated rings. In the case of (iii), the difference in electronegativity 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 aggregation states of the polymers.



**Scheme 1.** Chemical structures of poly(9,9-di-*n*-octylfluorenyl-2,7-diyl) (**PF8**), poly(9,9-di-*n*-octylsila-fluorenyl-2,7-diyl) (**PSi8**), poly(9-(1-octylnonyl)-9*H*-carbazole-2,7-diyl) (**PCz8**), **P(F8-*alt*-Si8)**, **P(F8<sub>0.80-ran</sub>-Si8<sub>0.20</sub>)**, **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 ( $\text{CHCl}_3$ ) as well as in aggregation states ( $\text{CHCl}_3$ /(*R*)-limonene (**1R**) or (*S*)-limonene (**1S**))/ $\text{CH}_3\text{OH}$ ). 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 ( $\text{CHCl}_3$ /(**1R** or **1S**)/ $\text{CH}_3\text{OH}$ ), 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  $\beta$ -phase in the tersolvents.<sup>3d</sup> The common  $\pi$ - $\pi^*$  absorption band near 400–410 nm and 350–360 nm is ascribed to the chiral  $\alpha$ -phase. For the PL emission, the intensities of all the polymers in aggregation states were relatively weaker than those in  $\text{CHCl}_3$  solution, which is due to the aggregation-caused quenching (ACQ) mechanism.<sup>4d</sup>

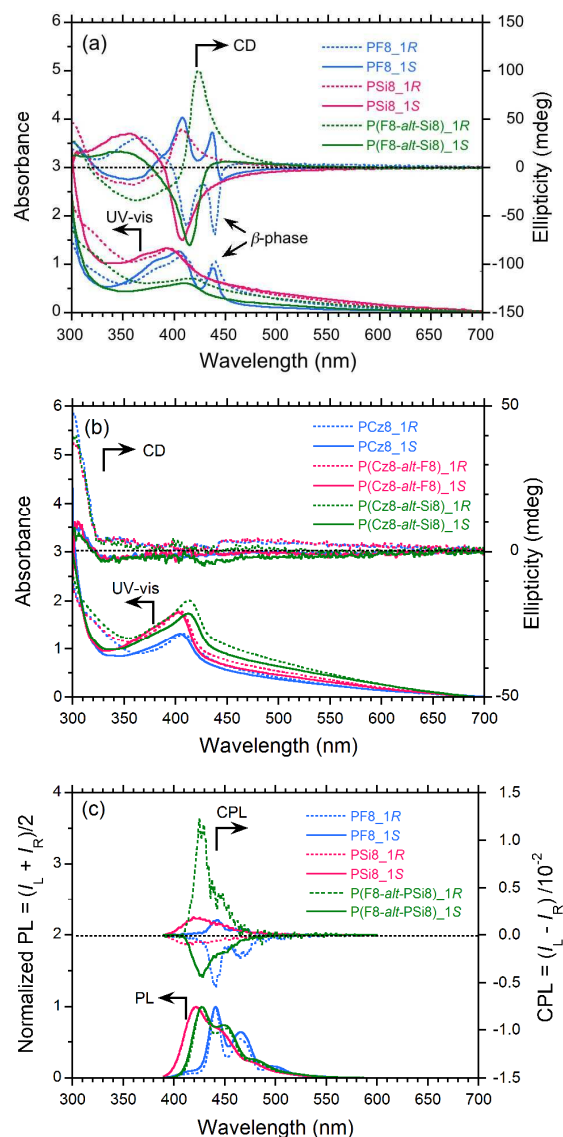
**Polymer Structure Dependency of Chiroptical Properties.** Our previous results demonstrated that the molecular weight of poly(9,9-di-*n*-decylfluorene) has obvious effect on the chiroptical properties.<sup>3d</sup> The current system is focused on the structure-dependency and mechanism of solvent-induced 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  $\text{CHCl}_3$ /(**1R** or **1S**)/ $\text{CH}_3\text{OH}$ . Additionally, UV-vis and CD spectra of **P(F8<sub>0.80-ran</sub>-Si8<sub>0.20</sub>)** are given in Figs. S2i, S2j, S4. All polymers did not show any Cotton CD signals in  $\text{CHCl}_3$ /(**1R** or **1S**) cosolvent in the absence of poor solvent, methanol, due to the lack of aggregation (Fig. S3), which agreed with previous reports.<sup>3</sup> The polymer solutions became turbid in mixed tersolvents ( $\text{CHCl}_3$ /(**1R** or **1S**)/ $\text{CH}_3\text{OH}$  = 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 CD extrema ( $\lambda_{\text{ext}}$ ) of seven polymer aggregates.

Polymers	Sign of Cotton effects / $\lambda_{\text{ext}}$ (nm)					
	$\text{CHCl}_3$ / <b>1R</b> / $\text{CH}_3\text{OH}$ system			$\text{CHCl}_3$ / <b>1S</b> / $\text{CH}_3\text{OH}$ system		
	$\beta$ -phase	$\alpha$ -phase1	$\alpha$ -phase2	$\beta$ -phase	$\alpha$ -phase1	$\alpha$ -phase2
<b>PF8</b>	(-)/438	(-)/412	(+)/357	(+)/436	(+)/408	(-)/354
<b>PSi8</b>	-	(+)/407	(-)/358	-	(-)/407	(+)/356
<b>PCz8</b>	-	-	-	-	-	-
<b>P(F8-<i>alt</i>-Si8)</b>	-	(+)/423	(-)/362	-	(-)/414	(+)/354
<b>P(F8-<i>alt</i>-Cz8)</b>	-	-	-	-	-	-
<b>P(Si8-<i>alt</i>-Cz8)</b>	-	-	-	-	-	-
<b>P(F8<sub>0.80-ran</sub>-Si8<sub>0.20</sub>)</b>	-	(-)/416	(+)/357	-	(+)/410	(-)/362

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  $\mu\text{m}$  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*-F8)** with **1R** and **1S** did not clearly provide such dot like FOM images. **PF8** aggregates in  $\text{CHCl}_3$ /**1R**/ $\text{CH}_3\text{OH}$  showed three distinct CD extrema in the region of the  $\pi$ - $\pi^*$  transition (Fig. 1a), which potentially can be attributed to the chiral  $\beta$ -phase (negative sign at 438 nm) and the chiral  $\alpha$ -phase (negative sign at 412 nm and positive sign at 357 nm), as reported earlier.<sup>3d,3j</sup> In opposite handed chiral solution,  $\text{CHCl}_3$ /**1S**/ $\text{CH}_3\text{OH}$ , **PF8** showed the opposite CD signal at a

similar wavelength as the  $\text{CHCl}_3/\mathbf{1R}/\text{CH}_3\text{OH}$  system. Both UV-vis and CD spectra confirmed the absence of  $\beta$ -phase in **PSi8** aggregate. All results are summarized in Table 1.



**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:  $\text{CHCl}_3/(\mathbf{1R}$  or  $\mathbf{1S})/\text{CH}_3\text{OH} = 0.3/1.2/1.5$  (v/v/v) for **PF8** ( $1.94 \times 10^{-2}$  mg mL<sup>-1</sup>) and **PSi8** ( $1.41 \times 10^{-2}$  mg mL<sup>-1</sup>), solvent fraction = 0.3/0.8/1.9 for **P(F8-alt-Si8)** ( $7.92 \times 10^{-3}$  mg mL<sup>-1</sup>). (b) UV-vis and CD spectra of **Cz8**-containing polymers in tersolvents at 25 °C. Conditions: solvent fraction = 0.3/1.2/1.5 for **PCz8** and 0.3/0.8/1.9 for **P(Cz8-alt-F8)** and **P(Cz8-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  $1.98 \times 10^{-2}$  mg mL<sup>-1</sup> 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<sub>0.80</sub>-*ran*-Si8<sub>0.20</sub>)** was similar

to that of **PF8**, and CD intensity of **P(F8<sub>0.80</sub>-*ran*-Si8<sub>0.20</sub>)** was much weaker than that of **PF8** (Figs. 1a and S4). On the other hand, the CD spectrum shape of **P(F8-alt-Si8)** 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 **Cz8**-containing homopolymer (**PCz8**) and its alternating copolymers (**P(F8-alt-Cz8)** and **P(Si8-alt-Cz8)**), 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 **Cz8**-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  $g_{\text{CD}}$  and  $g_{\text{CPL}}$ . 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  $\pi$ - $\pi^*$  CD bands. The magnitude of the  $g_{\text{CPL}}$  value ( $-5.2 \times 10^{-3}$  (**1R**)) is almost double of the corresponding  $g_{\text{CD}}$  values (*ca.*  $-2.0 \times 10^{-3}$  (**1R**)) from the 438-nm CD band. Similarly, the magnitude of the  $g_{\text{CPL}}$  value ( $+1.5 \times 10^{-3}$  (**1S**)) is slightly greater than that of the corresponding  $g_{\text{CD}}$  values (*ca.*  $+1.1 \times 10^{-3}$  (**1S**)) from the 438-nm CD band. If any significant structural change takes place in the ground and excited states, the  $g_{\text{CD}}$  value is expected to exhibit a different value, and in some cases, the sign inversion is possible. However, we evaluated that  $g_{\text{CD}} = [\text{Ellipticity (in mdeg)}/32980]/\text{Absorbance}$ , 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)**,  $g_{\text{CD}}$  and  $g_{\text{CPL}}$  values were  $+4.2 \times 10^{-3}$  (423 nm) and  $+1.2 \times 10^{-3}$  (426 nm) for the **1R** system, and  $-3.9 \times 10^{-3}$  (414 nm) and  $-0.4 \times 10^{-3}$  (428 nm) for the **1S** system. Note that, for **P(F8-alt-Si8)**, the absolute magnitudes of the  $g_{\text{CPL}}$  values are greatly decreased by at least one-third, compared to the corresponding  $g_{\text{CD}}$  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  $g_{\text{CPL}}$  but not to decrease it.

However, the disagreement in the sign of  $g_{\text{CPL}}$  and  $g_{\text{CD}}$  at the first Cotton bands was observed in **PSi8** aggregates. The  $g_{\text{CD}}$  and  $g_{\text{CPL}}$  values were  $+4.2 \times 10^{-3}$  (423 nm) and  $-0.4 \times 10^{-3}$  (428 nm) for **1R** system, and  $-3.9 \times 10^{-3}$  (414 nm) and  $+1.2 \times 10^{-3}$  (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,<sup>3</sup> we tested (1) seven poor solvents and (2) nine different solvent fractions in the  $\text{CHCl}_3/(\mathbf{1R}$  or  $\mathbf{1S})/\text{CH}_3\text{OH}$  system in more detail. Firstly, among the seven poor solvents, the absolute CD and  $g_{\text{CD}}$  values were maximized when most polar  $\text{CH}_3\text{OH}$  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  $\pi$ -conjugated polymers. Secondly, as expected, the relative volume fraction of methanol (poor solvent) and limonene (chiral source) clearly affected the absolute CD and  $g_{CD}$  values (Fig. S7). Both an abundant amount of poor solvent and chiral source result in inefficient limonene chirality transfer to the aggregates of above  $\pi$ -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 chiroptical device fabrications. Here again, the chiroptical inversion in the ground state between **PF8** and **PSi8** or **P(F8-*alt*-Si8)** was confirmed.

Nonlinear chiroptical amplification, well-known as the majority rule<sup>3c,3d,3f,3i,3j,3m</sup>, led us to further test a possibility of limonene enantiopurity dependency in a series of optically active **PF8**, **PSi8** and **P(F8-*alt*-Si8)** aggregate systems. These systems showed, however, no marked majority rule because CD amplitude and  $g_{CD}$  value alter almost linearly as a function of limonene enantiopurity (see, Fig. S8). This could be caused by a rapid growth in the aggregation process seeded by instant nucleation in the presence of poor solvent.<sup>3,7</sup> Similar enantiopurity dependency of the chiral solvents and additives was reported for the other CD active  $\pi$ -conjugated polymers and supramolecular  $\pi$ - $\pi$  stacks.<sup>3</sup> This also maintained the chiroptical inversion in the ground state between **PF8** and **PSi8** or **P(F8-*alt*-Si8)**.

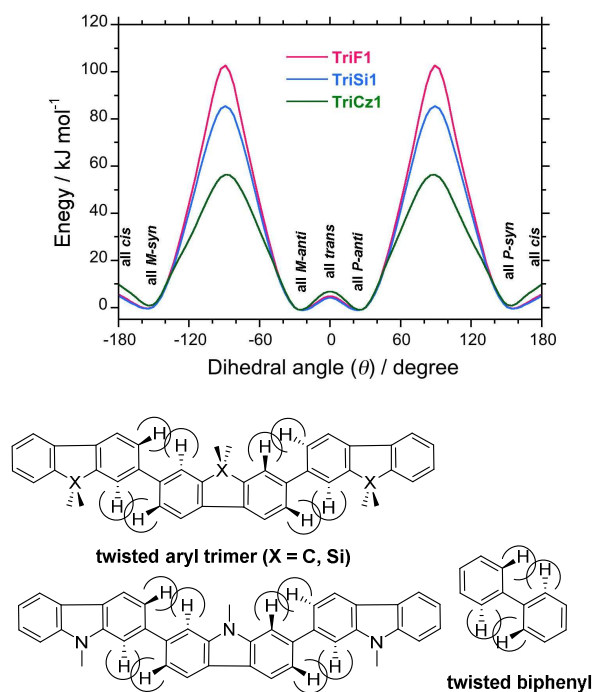
Furthermore, we investigated the polymer concentration dependency on the  $g_{CD}$ , which is known as a key factor in AICD systems.<sup>6</sup> Fig. S9 shows the  $g_{CD}$  values dependency on initial concentrations of **PF8**, **PSi8**, and **P(F8-*alt*-Si8)**. In optically active **PF8** and **PSi8** aggregates, the  $g_{CD}$  values increased almost linearly with the polymer concentration, and leveled off at constant values when the concentration of repeating polymer units (RPU) was greater than  $5 \times 10^{-5} \text{ mol L}^{-1}$  (Fig. S9e). Similarly, the  $g_{CD}$  value of **P(F8-*alt*-Si8)** increased almost proportionally to the concentration of RPU at lower concentrations ( $\leq 2 \times 10^{-5} \text{ mol L}^{-1}$ ). This is because the relatively low concentration results in production of loose  $\pi$ - $\pi$  stacked self-assembly in aggregates.<sup>3i,3j,8</sup> A similar phenomena has been reported by Tang's<sup>8c</sup> and our groups.<sup>3i,3j</sup> Conversely, the  $g_{CD}$  value of **P(F8-*alt*-Si8)** slightly decreased when further polymer concentration increased. Though the intensity was dependent on the concentration, the opposite sign of Cotton effect between **PF8** and **PSi8** or **P(F8-*alt*-Si8)** did not change. It is noteworthy that in most cases the CD and CPL patterns of the chiral aggregates of the polymers induced by **1R** and **1S** are not exact mirror images and that the positions and relative intensities are slightly different. A possible explanation of this phenomenon is that the slightly different aggregation behaviors resulted from slightly different solubilities in current tersetolvent systems.

### 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 chiroptical inversion between **PF8** and **PSi8** in aggregate states. For (2), it has been reported that chiroptical inversion in chiral oligomers/polymers,<sup>1e-g,9</sup> achiral molecules,<sup>2h,10</sup> polymers,<sup>3,11,12</sup> gel, and supramolecules<sup>13</sup> are susceptible to physical and chemical stimuli. However, such an element-dependent chiroptical inversion is relatively rare. We discuss the

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 ( $15^\circ$  interval including  $0^\circ$ ) between aromatic rings. To clarify why it favors twisted geometries, schematic drawing of aryl trimer and biphenyl is illustrated in Fig. 2 (bottom-left). Evidently, all **TriF1**, **TriSi1**, and **TriCz1** cannot adopt coplanar *trans* (dihedral angle  $\theta=0^\circ$ ) and *cis* ( $\theta=180^\circ$ ) 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  $\theta = \pm 30^\circ$  (*anti*-form) and local minima at  $\theta = \pm 150^\circ$  (*syn*-form). These inherent non-coplanar characteristics resemble the built-in nature of biphenyl to be twisted by  $\theta = \pm 30^\circ$  (Fig 2, bottom-right).



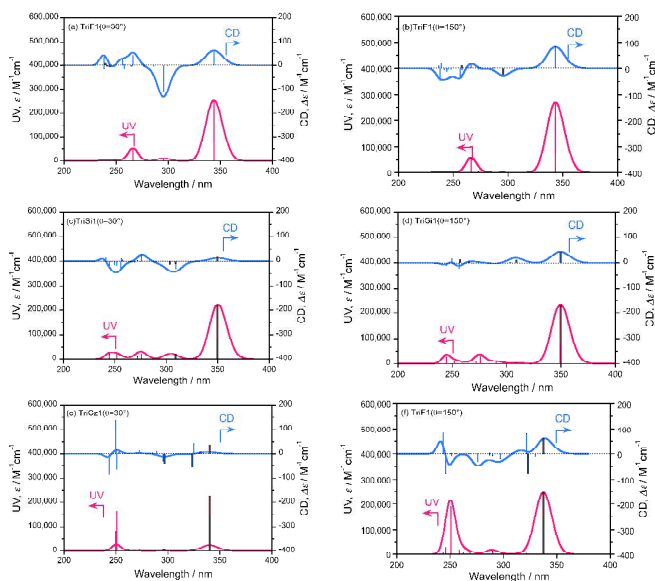
**Fig. 2** (top) Potential energy surface of 9,9-dimethylfluorene trimer (**TriF1**), 9,9-dimethylsilafluorene trimer (**TriSi1**), and *N*-methylcarbazole trimer (**TriCz1**) as a function of dihedral angle between aromatic rings obtained with DFT calculation (B3LYP/6-31G(d,p) level). Schematic pictures of inherently twisted geometries of aryl trimers (bottom, left) and biphenyl (bottom, right).

The energy difference between *anti*- and *syn*-forms is approximately  $0.65 \text{ kJ mol}^{-1}$  per number of dihedral angle. Rotational barrier heights ( $E_b$ ) between *anti*-forms at  $\theta = \pm 30^\circ$  are also small, where  $E_b$  per number of dihedral angle are **TriF1**  $\approx 2.4 \text{ kJ mol}^{-1}$ , **TriSi1**  $\approx 2.0 \text{ kJ mol}^{-1}$ , and **TriCz1**  $\approx 3.5 \text{ kJ mol}^{-1}$ . These low

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<sup>-1</sup>, **TriSi1**  $\approx 90$  kJ mol<sup>-1</sup>, and **TriCz1**  $\approx 57$  kJ mol<sup>-1</sup>. 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  $150^\circ$  (left handed) obtained with TD-DFT calculation (B3LYP/6-31G(d,p) basis set) are depicted in Fig. 3. The UV  $\lambda_{\max}$  and CD  $\lambda_{\text{ext}}$  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  $30^\circ$  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  $|g_{\text{CD}}|$  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.



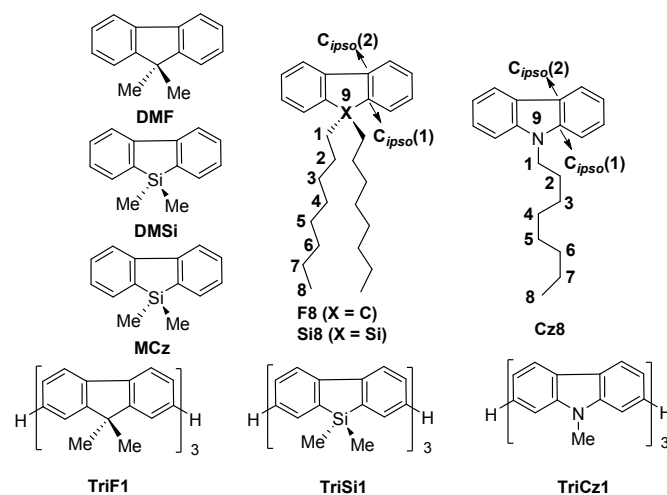
**Fig. 3** Simulated CD and UV spectra (with full width at half maximum (*fwhm*) of 0.1 eV) of (a, b) **TriF1**, (c,d) **TriSi1** and **TriCz1** at dihedral angles of  $30^\circ$  and  $150^\circ$  obtained with TD-DFT calculation (B3LYP/6-31G(d,p) level).

*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,<sup>3c</sup> among various non-polar and polar chiral sources, less-polar limonene and  $\alpha$ -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  $C_{\text{ipso}}(1)$  have  $-0.11$  and  $+0.30$ , whereas, for **Si8**, 9-Si and  $C_{\text{ipso}}(1)$  are  $+0.62$  and  $-0.12$ , which is opposite to the former. The switching in the charge between 9-C/9-Si and  $C_{\text{ipso}}(1)/C_{\text{ipso}}(1)$  may be related to the CD inversion between **PF8** and **PSi8** aggregates. We assume that **1R**, 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 **1R**, which has three stable equatorial rotamers (Fig. S12, Tables S2 and S3 and related discussion).<sup>13</sup>

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.



**Scheme 2.** Chemical structures of 9,9-dimethylfluorene (**DMF**), 9,9-dimethylsilafluorene (**DMSi**), *N*-methylcarbazole (**MCz**), 9,9-di-*n*-octylfluorene (**F8**), 9,9-di-*n*-octylsilafluorene (**Si8**), *N*-*n*-octylcarbazole (**Cz8**), 9,9-dimethylfluorene trimer (**TriF1**), 9,9-dimethylsilafluorene trimer (**TriSi1**), and *N*-methylcarbazole trimer (**TriCz1**) chosen for Gaussian03 (rev. E) calculations.

**Table 2.** Mulliken charges of selected atoms from **F8**, **Si8**, and **Cz8** in the ground and excited states taken from Figs. S10 and S11.

	State <sup>a)</sup>	Debye <sup>b)</sup>	$\pi$ -Ring				$n$ -Octyl chain(s)			
			9(X)	C <sub>pro</sub> (1)	C <sub>pro</sub> (2)	RingC1	C1	C2	C3	C8
<b>F8</b>	gs	0.27	-0.11	+0.30	+0.07	-0.12	-0.16	-0.18	-0.18	-0.32
	es	0.37	+0.93	+0.58	-0.50	-0.27	-0.09	-0.03	-0.37	-0.49
<b>Si8</b>	gs	0.30	+0.62	-0.12	+0.06	-0.14	-0.38	-0.18	-0.18	-0.32
	es	0.81	+0.81	-0.61	-0.32	-0.09	-0.17	-0.16	-0.26	-0.48
<b>Cz8</b>	gs	2.15	-0.65	+0.30	+0.04	-0.12	-0.06	-0.18	-0.18	-0.32
	es	2.02	0.00	-0.26	+0.44	-0.05	+0.15	-0.17	-0.19	-0.48

a) gs and es mean ground and excited states, respectively. b) Dipole moment.

## Conclusions

We have demonstrated a novel element-dependent chiroptical inversion and structural dependence of  $\pi$ -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 CHCl<sub>3</sub>/(**1R** or **1S**) cosolvent, in solution state. By inducing aggregation using the tersolvent system, CHCl<sub>3</sub>/(**1R** or **1S**)/CH<sub>3</sub>OH, chirality was successfully transferred to **PF8** and **PSi8** or **P(F8-alt-Si8)** aggregates. The opposite CD signal between **PF8** and **PSi8** or **P(F8-alt-Si8)** were detected in (i) several poor solvents, (ii) various volume fractions of limonene and CH<sub>3</sub>OH, (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  $\pi$ -conjugated polymers in aggregation states, which provides a new approach to the design of functional assemblies with chirality.

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## 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  $C_{ipso}(1)$  in **Si8** and  $C_{ipso}(1)$  in **F8**.

