

## Summary of Contents of Doctoral Thesis

### Title of Doctoral Thesis: **Aggregation-Induced Scaffolding of Helical Polysilanes: Instantaneous Generation of Optically Active Polyfluorenes**

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(Summary)

Recently, utilization of chiral scaffold to fashion CD-/CPL-silent molecules, oligomers, polymers into CD-/CPL-active organization is one of the hottest topics in supramolecular materials science. Generally, chiral molecules, oligomers and polymers allow for utilization of built-up to helical motif through weak intermolecular interactions.<sup>1,2</sup> Herein, the author showcased that non-charged artificial helical Si-Si bond polymers (PSi-*S* and PSi-*R*) can induce CPL- and CD-activities to non-charged, non-helical poly(9,9-di-*n*-octylfluorene) (PF8) in an aggregation state. The author found that PSi-*S* and PSi-*R* are beneficial as a versatile scaffold because they are easily removable by photocleavable reaction at Si-Si bond at 313 nm. My dissertation contains three sections: (1) Experimental results in proving the PSi helix scaffolding capability to PF8 before and after complete removal of PSi; (2) A possible mechanism of the PF8-PSi-*S* hetero-aggregate; (3) Several factors affecting the efficiency of the PF8-PSi-*S* hetero-aggregates, including the optofluidic effect, PSi-to-PF8 ratio, molecular weights of polymers, *n*-alkyl side-chain length of polymers, main-chain helicity of PSi, and extension to green color photoluminescent optically active poly[(9,9-di-*n*-octylfluorene-2,7-diyl)-*alt*-bithiophene] (PF8T2).

#### **1. Chirality amplification and removal of PSi scaffold from PF8**

The PF8-PSi-*S* hetero-aggregates revealed several intense CD bands arising from exciton couplet due to helically assorted PSi around 320 nm and  $\alpha$ -phase and  $\beta$ -phase of the chiral PF8 at 399 nm and 435 nm. This means the macromolecular helicity transfer from non-charged PSi to non-charged non-helical PF8 is possible. Moreover, based on my knowledge that PSi-*S* decomposes rapidly within 60 s, the author found that chirality of PF8 is retaining even after photocleaving reaction of Si-Si bond at 313 nm. This indicated that PSi efficiently acts as photochemically removable scaffold that enables to generate chiral PF8 when non-helical PF8 was employed as starting materials.

#### **2. PSi to PF8 scaffold structures and a possible mechanism**

Due to the high-sensitivity of PSi using TEM and SEM measurements, the author visualized the structures of PF8, PSi-*S*, and PSi-*S*-and-PF8 hetero-aggregates by DFM-AFM technique. From

several height profiles of DFM-AFM images, AFM height of P*Si-S* casting from pure chloroform solution ranged from  $\approx 0.5$  and  $\approx 1.1$  nm on HOPG. These heights were nearly consistent with diameters of individual P*Si-S* chains that laterally aligned on HOPG surface. On the other hand, PF8 adopted an ill-defined, highly entangling organized structures on HOPG, that include face-on, edge-on and loop-train-tail structures. Finally, height profiles of P*Si-S* and PF8 aggregates obtained with 5 % methanol and 95 % chloroform indicated that the aggregates had an almost uniform cross-section height ranging from 5.5 and 6.1 nm.

### 3. Factors affecting the ability of helix scaffolding of P*Si* to PF8

The cosolvent showed a great enhancement in the  $g_{CD}$  value of the hetero-aggregate at a specific  $n_D$  of  $\approx 1.41$  where the mixture of good and poor solvents (toluene and methanol) was 1 to 1 ratio (v/v). Surprisingly, P*Si*-and-PF8 hetero-aggregates preferentially adopt a stoichiometry 2-to-1 ratio. Besides, molecular weight of the polymers played a crucial role in providing sufficient chirality transfer. Nearly identical DP<sub>n</sub> values of P*Si-S* and PF8 afforded the highest  $g_{CD}$  amplitude that attains  $\approx -0.005$  at 438 nm of PF8. Moreover, n-alkyl side-chain length of both seven carbons for P*Si-S* and PF8 showed the highest  $g_{CD}$  value of  $\approx -0.012$  at 438 nm of PF7. However, further increase in side-chain lengths of both polymers, the  $g_{CD}$  amplitude decreased. Thus, the amplification of  $g_{CD}$  highly depended on the main-chain helicity of the scaffolding ability. Next, the author tested whether sergeant-soldier and majority rules are applicable to the current P*Si* scaffolding systems. When P*Si-R-ran-Pi-S* copolymers employed, P*Si-R-ran-Pi-S*-and-PF8 hetero-aggregates revealed majority rule effect that is similar to a polyisocyanate copolymers.<sup>3</sup> However, when P*Si-R(S)-ran-Pi-iBu* copolymers employed, anomaly in sergeant-soldier effect was found. Based on my finding, the author verified that P*Si* is transferable to non-helical PF8T2 as an aggregate form, as proven by CD and CPL spectra.

### References

- [1] Schwartz, E.; Stephane, L. G.; Cornelissen, J. J. L. M.; Nolte, R. J. M.; Rowan, A. E. *Chem. Soc. Rev.* **2010**, *39*, 1576.
- [2] Palmans, A. R. A.; Meijer, E. W. *Angew. Chem. Int. Ed.* **2007**, *46*, 8948.
- [3] Green, M. M.; Garetz, B. A.; Munoz, B.; Chang, H. P. *J. Am. Chem. Soc.* **1995**, *117*, 4181.

(論文審査結果の要旨)

近年、光学活性(高)分子により不斉誘導された円偏光信号(CD/CPL)活性な分子、オリゴマー、高分子材料の研究が活発化している。本研究では、紫外光で主鎖切断を起こす非荷電 $\sigma$ 共役ポリシラン(PS)をらせん誘起高分子、主鎖切断されない青色発光 $\pi$ 共役ポリフルオレン(PF)をCD/CPL不活性高分子として選択し、(1)PS-PF間のらせん転写特性、(2)PS主鎖切断前後の光学活性PFのCD/CPL特性把握、(3)Sergeant-and-soldier型、majority rule型CD/CPL増幅特性の把握、(4)他の $\pi$ 共役高分子への適用性を計画し、検証した。その結果、

(1) 非荷電らせん高分子と非荷電高分子間のらせん転写特性の検証

種々の(S)-/(R)-2-メチルブチル側鎖PS誘導体のらせん構造が、種々のn-アルキル側鎖PF類に効果的にらせん転写され、CD/CPL活性凝集体を与えることを見いだした。転写特性は、PFやPSiの分子量や側鎖長、PSi/PF組成比に大きく依存した。熱力学に準安定らせん状態から安定らせん状態への転移、そして不斉CH/HC相互作用などがらせん駆動力であると考察した。

(2) PS主鎖切断後の光学活性PFのCD/CPL特性

CD/CPL活性PS-PF共凝集体に紫外光を照射したところ、PS主鎖を選択分解しても、PFのCD/CPL特性は保持された。PSが光分解らせん足場高分子として有効に機能することを確認した。

(3) Sergeant-and-soldier型、majority rule型CD/CPL増幅特性

(S)-/(R)-キラル側鎖PSコポリマーをらせん誘起足場高分子としてPFにらせん転写実験を行った。その結果、これまで報告されてきたSergeant-and-soldier型、majority rule型CD/CPL増幅現象とは非常に異なる特異な現象を見いだした。

(4)他の $\pi$ 共役高分子への適用性

PS類が他の非荷電 $\pi$ 共役高分子へらせん誘起足場高分子として機能発現することを検証した。その結果、緑色発光F8T2を含む多くの高分子に対してらせん転写特性を与えることをCD/CPL分光法により実証した。

本研究は、非荷電 $\sigma$ 共役PSのらせん性が非荷電 $\pi$ 共役非らせん高分子に、非共有結合を介して転写され、PS除去後も転写らせんが保持されることを見いだした。その知見の、不斉科学、アストロバイオロジー、高分子科学、超分子科学など広範囲の学術領域への波及効果が期待される。よって審査員一同は本研究が博士(工学)の学位論文として価値あるものと認め、審査結果を合格と判定した。