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Journal Name

ARTICLE

Aggregation-induced scaffolding: Photoscissable helical polysilane generates circularly polarized luminescent polyfluorene

Nor Azura Abdul Rahim\textsuperscript{a,b} and Michiya Fujiki\textsuperscript{a,*}

An enantiopair of rigid rod-like helical polysilanes (PSI-S and PSI-R) as a photoscissible scaffold enabled the production of circularly polarised luminescence (CPL)- and circular dichroism (CD)-active di-n-octylpolyfluorene (PF8) aggregates associated with complete removal by PSI-selective photoscissoring at 313 nm. PF8 revealed a considerably high dissymmetry factor ($g_{\beta}$) of $(2-5) \times 10^{-3}$ at 435 nm due to chiral $\beta$-phase of PF8 after the 313-nm irradiation.

1. Introduction

The origin of biomolecular handedness on Earth is one of the greatest mysteries among geochemists and chiral scientists.\textsuperscript{1} A possible answer to this unresolved question has been lost due to the complete loss of fossil records at the molecular level. Nevertheless, one can assume that a trace amount of chiral molecular species may act as a scaffold leading to the L-D preferences in the primordial Era\textsuperscript{1-11} even though all molecular evidence has completely disappeared as a consequence of chemical and photochemical scissoring reactions.

However, in materials science, several biological and artificial helix scaffolds with adaptability towards other achiral/chiral molecular, oligomeric and polymeric resources because of rotational freedom along the C=C, C=O and C=N single bonds can be utilised to build-up helical architectures with desired functions.\textsuperscript{2,3} A representative cryoexample is triple-helix collagens in tissue engineering.\textsuperscript{24} Other polymeric and oligomeric materials, such as synthetic polymers, DNA, oligopeptides, polysaccharides, carbon nanotubes and aromatic foldamers, are candidates for chiroptical and other functional scaffolding.\textsuperscript{2b-2l,3} However, completely removing these scaffolds from the resulting helically hybridised skeletons while maintaining the designed functions is a difficult task because the C=C single-bond-based scaffolding ability is both chemically and photochemically strong due to the sum of the weak intermolecular interactions.

Certain organic gelators, that enable to generate helical inorganic motifs by sol-gel process with alkoxyxilanes and tetraethoxysilane, might be scaffolding because most of organic moieties are removable by calcination and carbonation at high temperatures (500–900°C).\textsuperscript{3a-3c} Alternatively, macromolecular helicity induced by chiral amines can be kept by replacing with achiral amines and amino alcohols at room temperature.\textsuperscript{21} The starting chiral amines sources are regarded as scaffolding. More recently, Liu et al. demonstrated that an amphiphilic L- or D-glutamyl gelator generates circularly polarised luminescence (CPL)- and circular dichroism (CD)-active $\pi$-conjugated polyfluorene analogs during gelation with the aid of hydrogen bonds and hydrophobic forces, followed by removal of the glutamate via washing with methanol at room temperature.\textsuperscript{3d} Also, helicity of cationic molecular assemblies in water inverts kinetically by changing molar ratio between D- and L-tartrates. However, the tartrate did not act as scaffolding because the induced helicity completely disappeared after removal of the tartrate.\textsuperscript{3a}

Shinkai et al demonstrated several helicity transfer experiments in water-DMSO cosolvent from non-charged helical polysaccharide (schizophyllan and curdlan) to CD-/CPL-silent anionic charge poly(fluorene-alkyl-phenylene) with non-stoichiometric 13-to-8 ratio as repeating units.\textsuperscript{2h-2k} This macromolecule-to-macromolecule complexation can instantly form the corresponding CD- and CPL-active $\pi$-conjugated polymers. Alternatively, cationic charge curdlan forms a complex with non-charged permethyloligosilane and single-walled carbon nanotubes.\textsuperscript{2k}

Herein, we questioned whether these approaches are applicable to complexation between two non-charged artificial polymers without specific intermolecular interactions. Actually, we reported several aggregation-induced CPL- and CD-active $\pi$- and $\sigma$-conjugated polymers induced by molecular chirality transfer of non-charged limonene, $\alpha$-pinene and alcohols.\textsuperscript{4} In these cases, all of the starting polymers, which are non-charged and devoid of stereogenic centres in their main chain and side chains, are CD-silent dynamic helical polymers because of their substantial rotational freedom, which has a
low barrier height on the order of 5–10 kJ mol\(^{-1}\). The optically active solvents are regarded as volatile chiral fluidic scaffolds that are removable at ambient temperatures.\(^{14}\) Multiple chiral intermolecular CH/π, π/π and London dispersion interactions are assumed to be responsible for the emergence of the aggregation-induced chiroptical polymers.\(^{4}\)

The helix scaffolding protocol involves two major steps. The first step is to concurrently aggregate photochemical Si–Si scissoring reaction that are removable at ambient temperatures.\(^{2}\) Multiple chiral helix scaffolding systems. The noticeable difference in the photoscissoring ability of \(\text{PSi-PF8}\) and \(\text{PSi-}\) \(\text{PSi-PF8}\) is typical of the aggregation-induced emission effect.\(^{5}\)

2. Experimental Section

2.1 Materials

2.1.1. Preparation of \(\text{PSi}\)
Poly(n-hexyl-(S)-2-methylbutylsilane) (\(\text{PSi-S}\)) and poly(n-hexyl-\(\text{R}\)-2-methylbutylsilane) (\(\text{PSi-R}\)) were prepared and characterised according to the provided electronic supporting information (ESI).

2.1.2. Fractionation of \(\text{PF8}\)

The achiral \(\text{PF8}\), which was obtained from Sigma-Aldrich Japan (Tokyo, Japan), with a PDI of 3.6 was fractionated by the addition of a poor solvent to a chloroform solution containing the \(\text{PF8}\). In the fractionation process, \(\text{PF8}\) was first dissolved in chloroform (Wako, special grade) followed by the gradual addition of isopropanol (IPA) and stirring until the aggregate precipitated in the stock solution. The polymer was then filtered with a Whatman\textsuperscript{®} PTFE 1.0 \(\mu\)m membrane filter. The remaining \(\text{PF8}\) on the filter was collected and dried in a vacuum oven overnight. Similar fractionation processes were repeated with higher-polarity solvents (i.e., ethanol and methanol) and, ultimately, distilled water. \(\text{PF8}\) with \(M_n\) of 78,400 with 1.8 PDI was chosen for this study.

2.1.3. Hetero-aggregation of fractionated \(\text{PF8}\) and \(\text{PSi}\)

Spectroscopic-grade toluene and chloroform (Daiendo, Kumamoto, Japan) as good solvents and methanol (Daiendo) as a poor solvent were added to produce an optically active hetero-aggregate in a 10 mm synthetic quartz (SQ)-grade quartz cuvette. The optimized volume ratio was 1:1, with the total volume content of mixed toluene and methanol being fixed at 3.0 mL. The molar ratio of the polymers in dissolved toluene was tuned according to the experimental requirements. The dissolved \(\text{PF8}\) was added to the cuvette, followed by the rapid addition of fractionated \(\text{PSi-S}\) (\(M_n = 75,800\), PDI = 1.3) or \(\text{PSi-R}\) (\(M_n = 73,900\), PDI = 1.4) to produce a well-mixed complex, and methanol was slowly added. Simultaneously, CD-UV-Vis and CPL-PL spectroscopic data were collected within several minutes after completion of the hetero-aggregation process.

2.2. Characterisation

2.2.1. Chiroptical analysis\(^{8,9}\)

The magnitude of CD in the ground state was calculated as \(g_{\text{CD}} = 2 \times (\epsilon_l - \epsilon_r) / (\epsilon_l + \epsilon_r)\), where \(\epsilon_l\) and \(\epsilon_r\) are the extinction coefficients for left and right circularly polarised light, respectively. Parameter \(g_{\text{CD}}\) was obtained as follows: \(\Delta \alpha' = (\text{ellipticity/}32,980)\)/ absorbance at the CD extremum of the hetero-aggregates. The degree of circular polarisation in the photosexcited state was defined as \(g_{\text{CPL}} = 2 \times (\alpha_l - \alpha_r) / (\alpha_l + \alpha_r)\) at the CPL extremum of the hetero-aggregates, where \(\alpha_l\) and \(\alpha_r\) are the output signals for left and right circularly polarized emission, respectively.

2.2.2. Refractive index of cosolvents
The refractive index ($n_0$) value was evaluated by the equation

$$n_{0,ave} = x n_{0,MeOH} + (1 - x) n_{0,toluene}$$

where $x$ is the volume fraction of MeOH in the cosolvent. The $n_0$ values of pure MeOH and toluene were used for this evaluation.

### 2.2.3 Number-average degree of polymerization

The main chain lengths of PF8, PSI-S and PSI-R were evaluated by the product of their monomer unit lengths and number-average degree of polymerization $DP_n = M_w/M_0$, where $M_w$ and $M_0$ are the number-average of molecular weight and the molecular weight of the monomer unit.

### 2.3 Instrumentation

The CD/UV-Vis spectra of the aggregate were recorded using a JASCO (Tokyo, Japan) J-820 spectropolarimeter with a Peltier-controlled equipment to control solution temperature. A scanning rate of 100 nm min$^{-1}$, a bandwidth of 2 nm and a response time of 1 s at 20 °C were used to simultaneously obtain the CD and UV-Vis spectra. The CPL/PL spectra were recorded at 20 °C on a JASCO CPL-200 spectrofluoropolarimeter with a Peltier-controlled equipment. A path length of 10 mm, scanning rate of 100 nm min$^{-1}$, bandwidth for excitation of 10 nm, bandwidth for monitoring of 10 nm, response time of photomultiplier tube of 2 s and single accumulation were applied during the measurements.

The dichlorosilane monomers and their starting source materials were characterised by $^{13}$C (75.43 MHz) and $^{29}$Si (59.59 MHz) NMR spectra in CDC$_3$ at 30 °C with a Varian Unity 300 MHz NMR spectrometer (now, as a member of Agilent Technologies (Palo Alto, California)) with tetramethysilane as the internal standard. The optical rotation at the Na-D line was measured with a JASCO DIP-370 polarimeter using a synthetic material. The optical rotation at the Na-D line was recorded at 20 °C on a JASCO CPL-200 spectrofluoropolarimeter with a Peltier-controlled equipment.

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### 2.4 Materials

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### 2.4.1 Dynamic force mode (DFM) imaging of atomic force microscopy

Atomic force microscopy (AFM) images of atomic force microscopy (AFM) were captured using a SPA 400 SPM unit (Surface Science Instruments, Inc., now, Hitachi High-Tech Science Corporation (Tokyo, Japan)) by dropping the aggregate suspension in a mixture of methanol and toluene (= 1/1 (v/v)) and by drop-casting dilute chloroform solutions of PF8 (0.5 x 10$^{-5}$ M), PSI-S (1 x 10$^{-6}$ M) and their mixtures in a mixture of methanol and chloroform (0.05–0.10 and 0.95–0.90 (v/v)). The deposited specimens were observed after the solvents were removed. Herein, we chose chloroform with a low bp (≈ 61 °C) in place of toluene with a high bp (= 110 °C) to obtain good AFM images of these aggregates on HOPG.

Wide-angle X-ray diffraction (WAXD) data were collected by a Rigaku RINT-TTR III/NM instrument (Tokyo, Japan) using an X-ray wavelength of 1.5418 Å, CuK$_\alpha$ radiation with Ni filter and 2θ = 0.05° interval scan and scanning speed of 2 deg min$^{-1}$. The instrument was operated at 40 kV and 25 mA. Specimens onto an Si-crystal substrate were prepared by mixing PF8 solid ($M_w$ = 78,400), PSI-S solid ($M_w$ = 75,800) and PSI-S-PF8 (≈ 2:1 molar ratio) hetero-aggregate from chloroform-methanol (1/1 (v/v)) and from toluene-methanol (1/1 (v/v)). These specimens were dispersed in a high vacuum silicone grease (Dow-Corning-Toray).

The aggregate sizes were analysed by an Otsuka Electronics DLS-6000 dynamic light scattering (DLS) system (Hirakata Osaka, Japan) with a detector angle of 90° and 30 accumulations using solution viscosity obtained with a Sekonic (Tokyo, Japan) viscometer VM-100 at 25 °C, along with the $n_0$ value of methanol-toluene (1:1 (v/v)) at 589 nm at 25 °C using an Atago (Tokyo, Japan) thermo-controlled DR-M2 refractometer at 589 nm (Tokyo, Japan) at 20 °C.

For cryo-TEM (transmission electron microscopy) analysis, the aggregate suspension in methanol-toluene (1:1 (v/v)) was drop-cast onto a JEOL carbon-coated copper grid in 200 mesh (Akishima-Tokyo, Japan) and then directly exposed to liquid nitrogen. The high-resolution HR-TEM images were obtained on a Philips Tecnai G2 F20 S-TWINN electron microscope operated at an accelerating voltage of 200 kV.

Computer generated pentamer model of PSI-S with P-73 helix (dihedral angle = 155°) and trimer model of PF8 (dihedral angle = 150°) were optimised with PM3-MM (Gaussian09 rev. D.01, Gaussian, Inc., Wallingford CT, 2013) running on an Apple PowerMac (2.67 GHz clock, 8-cores and 32 GB memory).

To measure the PL lifetime of PF8, we performed time-correlated single-photon counting (TCS-PC). The second harmonic (SHG = 420 nm) of a tunable Ti:sapphire laser (Coherent, Mira 900) with ≈ 150 fs pulse width and 76 MHz repetition rate was used as an excitation source. The PL emission was spectrally resolved using a collection of optics and a monochromator (Acton, SP-2150i). A TCSPC module (PicoHarp, PicoQuant) with an MCP-PMT (Hamamatsu, C4780) was used for ultrafast detection. The total instrument response function (IRF) for PL decay was less than 100 ps, which provided a temporal resolution of less than 10 ps. The deconvolution of the actual fluorescence decay and IRF was performed using fitting software (FlouFit, PicoQuant) to deduce the time constant associated with each exponential decay.

To photochemically decompose PSI-S (and PSI-R) in the PSI-PF8 hetero-aggregate suspension in a cuvette at room temperature, an ultra-high-pressure 500 W Hg lamp (Ushio (Tokyo, Japan), Optiplex BA-H501 and USH-500SC2) with a narrow band-pass filter of 313 nm (Asahi Spectra, Tokyo, Japan) was used. A photon flux at 313 nm was 14 µJ cm$^{-2}$ using an Si photodetector system (Ophir-Japan (Tokyo, Japan), Nova and PD300-UV). Details of the experimental set-up have been previously reported.

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3. Results and discussion

3.1 Chirality amplification from chiral PSi to achiral PF8

Fig. 2a shows the CD signals and broader UV-Vis spectra at approximately 399 nm that arise from \( \alpha \)-phase PF8. The longest CD band and a sharper visible band at 435 nm were assigned to \( \beta \)-phase PF8.40,44 An intense bisignate CD band at 305 and 322 nm was characteristic of exciton couplet arising from the helically assorted PSi aggregate.4c,8b

Our results indicate that the macromolecular helicity transfer is possible between helical non-charged PSi and non-helical non-charged PF8 during the course of hetero-aggregation using a toluene-methanol cosolvent. For comparison, chloroform-methanol cosolvents with several ratios were possible to generate CD-/CPL active PSi-PF8 hetero-aggregate though the absolute \( g_{\text{CD}} \) values of PF8 slightly weakened. The helix scaffolds of PSi-S and PSi-R have a similar \( M_n \) of \( \approx 26,000 \) and exhibit nearly ideal mirror-image CD spectral characteristics with optically active PF8, in agreement with the characteristics previously reported for analogous chiral polymer systems.2,4b,6 The coexistence of highly emissive \( \alpha \)- and \( \beta \)-phase PF8 in the aggregates led to the detection of clear CPL signals and PL spectra arising from the \( \beta \)-phase,4b,6 obeying a photoexcited energy migration scheme (ESI, Fig. S12). The CPL- and PL-bands are assigned to vibronic 

\begin{align*}
\nu &\approx 1470–1490 \text{ cm}^{-1} \\
\nu &\approx 305, 322 \text{ nm} \\
\nu &\approx 401 \text{ nm}
\end{align*}

(ESI, Fig. S12). The CPL- and PL-bands are assigned to vibronic spacing due to aromatic ring stretching vibration of chiral \( \beta \)-phase,3a,4b,6 as a result of spontaneous relaxation from the lowest \( S_1 \)-state with \( \nu = 0' \) to the \( S_2 \)-state with \( \nu = 0,1,2 \) by the Kasha’ rule.

3.2 Removal of PSi-S and PSi-R scaffolds

To spectroscopically elucidate the scaffolding capability of PSi-S and PSi-R toward PF8, the \( g_{\text{CD}} \) value of the hetero-aggregate suspension in a methanol-toluene cosolvent (1.5/1.5 (v/v)) with [PF8] = 2.5 \( \times 10^{-7} \) M and [PSi-S] = 5.0 \( \times 10^{-6} \) M as their repeating units. The \( M_n \) values of PSi-S, PSi-R and PF8 are 75,800, 73,900 and 78,800, respectively.

For further verification, a PL decay experiment of the PSi-S-PF8 hetero-aggregate before and after photoscission was employed (Fig 4a). The PL decay curve due to \( \beta \)-phase PF8 and its PL lifetime (\( \tau_{\text{PL}} \) detected at 480 nm) were nearly unchanged before and after PSi-PF8 selective photoscissoring at 313 nm for 600 s. The \( \tau_{\text{PL}} \) value was slightly delayed from 2.37 to 2.46 ns. This result indicates that PF8 maintained its original main chain structures even after prolonged UV irradiation, which resulted in photochemical removal of PSi-S as scaffolding. However, a helically assorted higher-order structure of PF8 remained unchanged and was stable during the photochemical reaction.

The results of a DLS study strongly supported this conclusion (Fig 4b). The hetero-aggregates caused division into two particles that were \( \approx 2,000 \) nm (\( \approx 40 \% \) by volume, relative to the original) and \( \approx 300 \) nm in diameter in a fashion. This feature is similar to a cell division process even though the band due to PF8 keto form (Fig. 3b).10 As evident in Fig. 3a, PSi-S decomposed rapidly within 60 s and completely disappeared within 300 s. The CD and CPL (Fig. 3b) amplitudes for PF8 in PSi-S-PF8, which was photoirradiated for 600 s, nearly retained their initial \( g_{\text{CD}} \) (approximately \( \pm 0.005 \) at 401 nm) and \( g_{\text{CPL}} \) (approximately \( \pm 0.004 \) at 438 nm) magnitudes along with the chiroptical signs of PF8 in the non-irradiated PSi-PF8 (=2:1) aggregates. An approximately 10–20 % decrease in the \( g_{\text{CD}} \) magnitudes of PF8 was observed after complete removal of PSi-R and PSi-S. The PSi-selective photoscissoring reaction of the PSi-PF8 hetero-aggregates was possible.
original material consisted of a single aggregate with a diameter of ≈ 2,730 nm. The 40 % reduction by volume was nearly equal to 49 % PF8 by weight in the original PSi-S-and-PF8 with a 2-to-1 ratio by repeat unit. The scissoring product of PSi-S was assumed to be mostly concentrated in the 300 nm particles, whereas PF8 mostly remained in the 2,000 nm particles. This result should provide a speculation that certain chiral species exist as sacrificial scaffolds in chemical evolution process of life and may catalyse the L-D preferences of biopolymers in μm-sized aggregate surrounded by aqueous medium,\(^1\) that is a model of coacervate coined by Oparlin and Haldane.

![Image](https://example.com/image.png)

**Fig. 4.** (a) PL lifetime at 420 nm (excited by 150-fs pulse laser) of hetero-aggregates made of PF8 (2.5 × 10\(^{-5}\) M) and PSi-S (5.0 × 10\(^{-5}\) M). (b) DLS data of the photobleached aggregates of PF8 (2.5 × 10\(^{-5}\) M) and PSi-S (5.0 × 10\(^{-5}\) M) in a toluene-methanol cosolvent (1.5/1.5 (v/v)) before and after irradiation at 313 nm (14 µJ/cm\(^2\)) for 600 s.

3.3 Optofluidic effect revealed as chiroptical amplification\(^4,9\)

The cosolvent was optimised by optofluiddically tuning \(n_0\) value and showed a great enhancement in the \(g_{CD}\) value of the hetero-aggregate at a specific \(n_0\) of ≈1.41 (Fig. 5), where the mixture of good and poor solvents (toluene and methanol) was 1 to 1 ratio (v/v). The detail of PSi-S CD-spectra was shown in ESI, Fig. S13. We are aware of the fact that the \(g_{CD}/n_0\) relationship shows a broad distribution for chiral PSi induced PF8 particle. This indicates that PSi-S and PF8 aggregate adopts a stable shape over a wide range of poor to good cosolvents.\(^11\)

![Image](https://example.com/image.png)

**Fig. 5.** The \(g_{CD}\) value of PF8 at 401 nm in Toluene-MeOH cosolvents as a function of the refractive index \((n_0)\) in the hetero-aggregate of the PSi and PF8 molar ratio is \(= 5.0 \times 10^{-5}\) M and \(2.5 \times 10^{-5}\) M. The \(M_1\) values of PSi-S, PSi-R and PF8 are 75,800, 73,900 and 78,800, respectively.

However, improper ratio of good and poor solvents in the optofluidic medium may cause instability of the aggregate structures. Similar effect has been discussed in π-conjugated polymer, molecules and supramolecular polymer self-assembly systems experimentally and by computational modeling.\(^12\)

3.4 Polymer molar ratio dependence

To gain additional insight into whether intermolecular interactions between PSi-S (PSi-R) and PF8 are stoichiometric, a Job's plot\(^13\) was constructed for the PSi-PF8 aggregates because such plots are useful for evaluating supramolecular complexes and applicable to polymer-polymer supramolecular complexes.\(^2,14,15\) The \(g_{CD}\) value at the second Cotton band (401 nm) as a function of the molar ratio (as repeating unit) of PF8/[PF8+PSi-S]/PSi-R is shown in Fig. 6a.

Surprisingly, the PSi-S-and-PF8 (and PSi-R-and-PF8) hetero-aggregates preferentially adopt a 2-to-1 PSi-PF8 ratio because the \(g_{CD}\) values reached a maximum at PF8/[PF8+PSi-S] and PF8/[PF8+PSi-R] of approximately 0.33. The hetero-aggregates do not obey the sergeant-and-soldier principle that is often observed in π-π stacked supramolecules and stiff helical copolymers.\(^14,16\) Further analysis of the Job's plot indicated that the PSi-PF8 hetero-aggregate is a supra-macromolecular complex with a 2-to-1 ratio (by repeating units) when the concentration of PF8 is fixed to be \(2.5 \times 10^{-5}\) M (Fig. 6b). The 2-to-1 ratio is equivalent to 51:49 (by weight).

Recently, spontaneous generation of a similar supramacromolecular triplex (so-called "stereocomplex") consisting of isotactic (i)- and syndiotactic (s)-poly(methyl methacrylate) (PMMA) with a 2-to-1 ratio was confirmed by HR-AFM and X-ray structural analyses.\(^14\) The stereocomplex on HOPG, however, may exist as a mixture of left- and right-handed triple helices.

Notably, PSi-S and PSi-R, in particular, adopt a rigid rod-like helical global conformation with high viscosity indices (\(\alpha = 1.24\) for PSi-S and \(\alpha = 1.52\) for PSi-R) in toluene (ESI, Fig. S9–S11), which were confirmed by an extremely long persistent length that was as long as 85 nm (≈ 450 Si-repeating units, molecular mass of 96,000) in THF among a family of polysilanes.\(^14\) However, PF8 adopts a semi-flexible CD-silent
helical conformation with substantial rotational freedom along the C–C bonds between the fluorene rings in the fluidic toluene solution. This result was confirmed by shorter persistent lengths of 10 nm at 25 °C and longer 34 nm at 50 °C. The combination of a highly rigid rod-like helix and semi-flexible CD-silent helical conformation may be critical for designing aggregation-induced scaffolding systems.

**3.5 Molecular weight dependence of helix scaffolding ability**

Well-designed supramolecular architecture can promote a well-defined molecular interaction when the two bodies are adhering together. This interaction should be closely related to spontaneously an assembling process. To clarify whether $M_n$ values of PF8 and PSi values affect the PSi-and-PF8 scaffolding capability, we examined the $g_{CD}$ value of PSi-and-PF8 with 2-to-1 hetero-aggregates as functions of $M_n$ values of PF8 and PSi-S in detail. Four PF8 samples with $PDI \approx 1.7$–2.0 and six PSi-S samples with $PDI \approx 1.3$–1.5 were isolated by an ordinary fractionation method with IPA, ethanol and methanol as precipitating solvents (Tables 1 and 2). For comparison, one PSi-R sample with $PDI \approx 1.3$ was used.

From irradiation time dependence at 313 nm to PSi-S-PF8 aggregates, the $g_{CD}$ value of the hetero-aggregates greatly depended on $M_n$ value of PSi-S when PF8 with $M_n = 82,800$ was fixed (Fig. 7a). It is evident that, among six PSi-S samples, the $g_{CD}$ value afforded the maximum one when PSi-S is $M_n = 40,500$ before and after the 313-nm irradiation. Thus, the $g_{CD}$ value did not monotonically increase as $M_n$ value of PSi-S increases (Fig. 7b). The scaffolding capability is crucial in providing an ideal intermolecular interaction between PF8 and PSi-S. On the other hand, the $g_{CD}$ value of PSi-S-PF8 aggregate monotonically increases and tends to reach level-off $g_{CD}$ values when the $M_n$ value of PSi-S ranges from 9,800 and 80,400 (Fig. 7c). The $g_{CD}$ value of PSi-S-PF8 aggregate weakly depends on $M_n$ value of PF8.

A pair of two different linear polymers with the oppositely charged pairs may promote a better electrostatic interaction as their main-chain lengths increase, due to sufficient intermolecular locking. However, in the case of pair of non-charged polymers, the semi-flexible PF8 may gradually loose the wrapping capability toward rod-like PSi-S above the critical $M_n = 80,000$. On the other hand, rod-like PSi-S efficiently acts as an efficient scaffold toward semi-flexible PF8 regardless of $M_n$ of PSi-S ranging from 9,800 and 80,400. The scaffolding
ability of PSI-\(S\) is kept during photochemical scissoring reaction of Si–Si bonds.

To further consider which factor among molecular weight, main-chain length and \(DP_n\), is critical factor to afford the best scaffolding ability and to discuss the reason why the best PSI-S-PF8 aggregate with the greatest \(g_{DD}\) value prefers the 1-to-2 ratio as repeating units (Fig. 6), we evaluated main chain lengths and \(DP_n\) values of PF8, PSI-\(S\) and PSI-\(R\) from the corresponding \(M_n\) values (Tables 1 and 2).

### Table 1. Molecular weights, polydispersity, main chain length and number-average degree of polymerization of PF8.

<table>
<thead>
<tr>
<th>Fraction</th>
<th>(M_n)</th>
<th>(M_n/M_w)</th>
<th>Length of PF8 (in nm)</th>
<th>(DP_n)</th>
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<tr>
<td>1</td>
<td>89,800</td>
<td>2.0</td>
<td>194</td>
<td>230</td>
</tr>
<tr>
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<tr>
<td>4</td>
<td>59,500</td>
<td>1.7</td>
<td>129</td>
<td>152</td>
</tr>
</tbody>
</table>

### Table 2. Molecular weights, polydispersity, main chain length and number-average degree of polymerization of PSI-\(S\) and PSI-\(R\).

<table>
<thead>
<tr>
<th>Chiral centre</th>
<th>(M_n)</th>
<th>(M_n/M_w)</th>
<th>Length of PSI (in nm)</th>
<th>(DP_n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>80,400</td>
<td>1.4</td>
<td>57</td>
<td>436</td>
</tr>
<tr>
<td>S</td>
<td>75,800</td>
<td>1.5</td>
<td>54</td>
<td>411</td>
</tr>
<tr>
<td>R</td>
<td>73,900</td>
<td>1.3</td>
<td>53</td>
<td>401</td>
</tr>
<tr>
<td>S</td>
<td>40,500</td>
<td>1.5</td>
<td>29</td>
<td>220</td>
</tr>
<tr>
<td>S</td>
<td>27,400</td>
<td>1.4</td>
<td>20</td>
<td>149</td>
</tr>
<tr>
<td>S</td>
<td>17,100</td>
<td>1.3</td>
<td>12</td>
<td>93</td>
</tr>
<tr>
<td>S</td>
<td>9,800</td>
<td>1.5</td>
<td>7</td>
<td>53</td>
</tr>
</tbody>
</table>

The stoichiometry as repeating units of PF8 and PSI is a critical factor for the hetero-aggregate, in which PF8 with \(DP_n\) ≈ 212 matches PSI-\(S\) with \(DP_n\) ≈ 220 in the range of \(DP_n\) = 50 and 436. CD- and UV-vis spectra of the PSI-S-PF8 aggregate were provided in ESI, Figs. S16a and S16b. Actually, the nearly identical \(DP_n\) values of PSI-\(S\) and PF8 afforded the highest \(g_{DD}\) amplitude that attains \(\approx 0.005\) at 438 nm of PF8.

Previously, Harada and Kataoka\(^{18}\) demonstrated that a precisely controlled main chain length of charged polymers helps to produce a highly ordered supramolecular assembly, resulting in a core-shell structure. In addition to main chain length, they found that the degree of polymerization (\(DP\)) plays a key role in constructing the self-assembling structure with the oppositely charged polymers, that is polyeon complex. In this case, all the polymers had an extreme narrow \(PDI < 1.1\). Their knowledge and understanding might be applicable to supramolecular complexation between two non-charged PF8 and PSI. The best matched \(DP_n\) values between PF8 and PSI is responsible for the supramolecular hetero-aggregation. This idea could be applicable to complexations between two polar polymers and between nonpolar polymers, as well as between the oppositely charged polymers.

An open question is why the 2-to-1 ratio is the best for the PSI-S-and-PF8 aggregates. Noted that each PF8 repeating unit has two \(n\)-octyl side chains at 9.9-position (eight carbons \(\times 2 = 16\) carbons), whilst each PSI-\(S\) repeating unit has single \(n\)-hexyl side chain (six carbon \(\times 1\)). A plausible answer is that two \(n\)-octyl side chains of PF8 repeating unit interact with two units of PSI-\(S\) carrying one \(n\)-hexyl side chain, enabling an efficient interaction of these \(n\)-alkyl side chains. To build a supramolecular structure, more longer alkyl side chains of polyfluorene derivatives will be needed to efficiently wrap around the rigid rod-like PSI-\(S\) helical main chains.

### 3.6. WAXD study of PSI-\(S\), PF8 and PSI-\(S\)-and-PF8 with 2:1 ratio

We compared the WAXD profiles between PSI-S-PF8 (1:2) hetero-aggregate and the corresponding PF8 and PSI-\(S\) homo-aggregates (Fig. S14, ESI). The WAXD profile of PSI-S-PF8 hetero-aggregate had three characteristic \(d\)-spacing at 4.4 Å, 7.5 Å and 12.4 Å. The 12.4 Å spacing is ascribed to interchain distance of PSI-\(S\). However, the origin of 4.4 Å and 7.5 Å spacing is obscure because these are commonly seen among three aggregates. However, the WAXD profile of PSI-S-PF8 hetero-aggregate subtly depended on sample preparation condition whether the aggregate was casted from toluene-methanol (1/1 (v/v)) or chloroform-methanol (1/1 (v/v)) (Fig. S15, ESI). The 12.4 Å spacing became 12.2 Å when chloroform was employed. The 7.5 Å spacing shortened by \(\approx 0.8\) Å and became \(\approx 6.7\) Å when chloroform was employed. The 4.4 Å spacing was unchanged.

The reductions of 0.2 Å and 0.8 Å in the hetero-aggregates implied certain interactions between PF8 and PSI-\(S\), depending on solvent condition. However, we did not obtain more useful information about these aggregates due to limited availability of clear X-ray scattering peaks. Helical pitch of polymers is susceptible to external physical and chemical biases. Recently, Knaapila et al reported that high hydrostatic pressure largely affects helical pitch of poly[9,9-bis(2-ethylhexyl)fluorene].\(^{10d}\)

### 3.7. TEM and AFM studies of PSI-\(S\), PF8 and PSI-\(S\) and PF8

We attempted to view the detailed structures of PF8 and PSI-\(S\) homo-aggregates and PSI-S-and-PF8 hetero-aggregates using cryogenic transmission electron microscopy (cryo-TEM) (ESI, Fig. S17). Because of rapid scissoring reaction of the Si–Si backbone over the TEM observation time, clear visualisation was impossible even at liquid-nitrogen temperature. Then, we employed DFM-AFM study because of no sample damage.

The first approach was to view DFM-AFM images of PSI-\(S\) and PF8 homo-aggregates and PSI-S-and-PF8 hetero-aggregates. These specimens were directly deposited onto HOPG by drop-casting the aggregates suspension in \(10^{-4}\) M toluene-methanol (1/1 (v/v)). However, we did not obtain clearer assorted images (ESI, Fig. S18).

The second approach was to use chloroform as a good solvent including a small volume fraction of methanol. We
obtained better resolution AFM images of PSI-S and PF8 homo-aggregates on HOPG by a drop-cast of their very dilute chloroform solutions (10⁻⁵ M) (ESI, Fig. S19–S22). Similarly, PSI-S-and-PF8 hetero-aggregate (as nominal ratio of 2-to-1) was casting from their dilute solution (≈ 10⁻⁷ M) of 5 % methanol and 95 % chloroform (ESI, Fig. S23). The choice of volatile chloroform was the key to yield better AFM images rather than less-volatile toluene.

From several height profiles of Fig. S19 in ESI, diameters of PSI-S casting from pure chloroform solution ranged from ≈ 0.5 and ≈ 1.1 nm on HOPG. These heights are nearly consistent with diameters of individual PSI-S chains that laterally aligned on HOPG surface. Two representative molecular diameters of 7₁-helical PSI-S were given in Fig. S19 in ESI. One motif is stretch out structure of n-hexyl side groups with all-trans geometry and the other one is its shrunk shape with gauche form. The height value of 1.1 nm is nearly identical to d-spacing (12.2 and 12.4 Å) of PSI-S solid (ESI, Figs. S15 and S16). A combined data of the WAXD and AFM images suggested that n-hexyl groups adopt the shrunk geometry on HOPG. An averaged end-to-end distance of PSI-S arrays on HOPG was ≈ 31 nm. This value corresponds to ≈ 170 Si-repeating units, but is one-third of DP₄ (= 458) evaluated by GPC analysis (Table 2). However, we could not clearly view a helical molecular image of PSI-S on HOPG. This is probably due to an AFM tip broadening effect since the current AFM tip size (2-5 nm) was largely depended on the initial volume fraction of methanol. Plausible helically assorted PSI-S on HOPG was illustrated in Figs. S20 and S21 in ESI.

On the other hand, height profiles of PF8 obtained with from 5 % methanol and 95 % chloroform ranged from ≈ 0.5 nm and = 2 nm (ESI, Fig. S22). When one can assume stretch out structure of two n-octyl groups with all-trans geometry, an estimated end-to-end distance of two side groups is ≈ 2.0 nm and thickness of PF8 rings is ≈ 0.5–0.7 nm. Because of semi-flexible nature, PF8 chains can turn into ill-defined, highly entangling organization on HOPG, including face-one, edge-on and loop-train-tail structures as outlined in ESI, Fig. S22, bottom right.

Finally, height profiles of PSI-S and PF8 aggregates obtained with 5 % methanol and 95 % chloroform tells us that the aggregates had an almost uniform cross-section height ranging from 5.5 and 6.1 nm (ESI, Fig. S23). These images suggested that PSI chains and PF8 chains spontaneously co-aggregated with 2-to-1 ratio on HOPG during co-evaporation of chloroform and methanol. The AFM images are not segregated structures of PSI and PF8. The height of ≈ 6 nm corresponds to two PSI chains interacted with two n-octyl groups of two PF8 chains, as illustrated in ESI, Fig. S24, top.

Additionally, we viewed two heights of ≈ 1.5 nm and ≈ 3 nm, depending on position of AFM tip. These heights may be ascribed to two PSI chains and two PSi chains with one-side of one PF8 chain, respectively (ESI, Fig. S24, bottom). Although we cannot obtain a clear helical AFM image of the hetero-aggregates, several alkyl side chains between PSI and PF8 are assumed to be interdigitated and coagulated. In this case, we postulated that two helical PSI-S chains form a double strand that is loosely wrapping by one PF8 chain. The double strand PSI-S is responsible for the intense exciton couplet CD signals at 310–320 nm (Fig. 2 and ESI, Fig. S25). From the AFM images, the twisted, but more planarised PF8 aggregate suspension in the cosolvents might be responsible for CD-/CPL-active β-phase at 434 nm (Fig. 2 and ESI, Fig. S26).

3.8 Possible interactions between non-charged PSI and PF8

Two unanswered questions still remained: (i) Does the CPL- and CD-activities of the PSI-selective photobleached PF8 aggregates arise from intermolecular covalent bonds with a photodecomposed moiety of PSI or from only non-covalent interactions? And (ii) what type of intermolecular interactions...
between PF8 and Psi is responsible for the scaffolding capability?

To address the first question, we measured the CD and UV-Vis spectra of a homogeneous chloroform solution containing photobleached aggregates of PSI-S-PF8 (=2:1). Figs. 8a-8b show the CD and UV-Vis spectra of the photobleached aggregates (313 nm, 60 s) of PSI-S-PF8 (=2:1) by adding chloroform; for comparison, the spectra of the corresponding original and photobleached PSI-S-PF8 aggregates in toluene-methanol cosolvent (1.5/1.5 (v/v)) before and after 313 nm irradiation for 60 s are also shown. The CD and UV-Vis bands of the α-phase (= 350 and ≈400 nm) and β-phase (= 433 nm) of PF8 completely disappeared in chloroform. Intermolecular crosslinking reactions did not occur in the aggregate during the photosorssoring process. The predicted silyl crosslinking reactions did not contribute to the maintenance of the CD and CPL activities in the PSI-S-PF8 aggregate.

Regarding the second question, we assume that H/H interactions (coined dihydrogen bonds) exist in the dimer of the saturated hydrocarbons as an extension of CH/π and London dispersion interactions.21 This proposal was based on rigorous calculations at the second-order Möller-Plesset (MP2) level with the 6-311+G(3df,3pd) basis set. In methane dimers, the stabilization energy arises from the weakly charged C⁻H⁻'H⁻C' pair in the valence bond; in particular, the positioning of the neighbours is critical. Staggered and eclipsed triple H/H contacts of the CH₂/H/C pair had a dissociation energy of 1.6–1.8 kJ mol⁻¹, and the staggered and eclipsed double H/H contacts of the CH₂/H/C pair had a dissociation energy of 1.0–1.4 kJ mol⁻¹.20

However, in n-alkane dimers, a staggered supramolecule with 3:3 and 1:1 contacts asymptotically stabilises as the methylene number increases. The dissociation energy plateaued at six methylenes, reaching 1.56 and 2.40 kJ mol⁻¹, respectively.20

Recently, Hariharan et al. reported experimentally and computationally that, in crystals of pyrenes substituted with acetyl and anthracene groups, the attractive H/H interactions between sp² C–H of pyrene and sp³ C–H of methyl (from of acetyl) and between sp² C–H of pyrene and sp³ C–H of anthracene with help of CH/π interaction facilitate to generate specific organisations such as herringbone, brickwork and columnar structures.21 These fascinating outcomes led us to propose that the minimal carbon number in the n-alkane dimer is six. Therefore, multiple attractive C-H/C interactions between the two n-octyl groups (PF8) and the n-hexyl group (PSI-S and -R) are sufficiently strong for scaffolding capability, irrespective of the absence of electrostatic, hydrogen-bonding, dipole-dipole, CH/π, CH/N, CH/O and π/π interactions. Our preliminary study indicated the best n-alkyl side-chain length pair between PF8 and PSI exists, enabling a more enhanced scaffolding capability with high g_{\alpha} values.

Various supramolecular polymer complexes using single- and two-components of molecular and oligomeric building blocks are promising to design (chir)optical, semiconducting, and biological functions as well as well-defined, higher-order fibrous and gel structures.22 Rather directional, intense hydrogen, π-π stacking and electron donor-acceptor interactions are driving forces for these well-defined, higher-order fibrous structures.

As demonstrated in this work, even non-directional weak interactions can contribute to supra-macromolecular complexation comprising non-charged, non-polar π- and σ-conjugated polymers though the resultant hetero-aggregate had a difficulty to characterize a detailed structure due to ill-defined structures. Nevertheless, our approach is beneficial to more freely design solution processible supra-molecular complexation of two non-charged macromolecules with sophisticated (chir)optical, electronic and other functions.

Actually, in a series of preliminary experiments, we confirmed that the aggregation-induced scaffolding with PSI-S and PSI-R is valid for commonly generate CD- and CPL-active π-conjugated polymers including poly[(9,9-di-n-octylfluoren-2,7-diyl)-alt-bithiophene] (PF8T2), poly[(9,9-di-n-octylfluoren-2,7-diyl)-alt-yleneethynylene] (PPE), poly(9,9-di-n-octylfluoren-2,7-vinylene) (PFV), and so on. Even PPE converted into the corresponding CD-/CPL-active aggregates with help of PSI-S though limonene was inefficient as the chiral liquid scaffold.20 The works are currently in progress.

3.9 Hetero-aggregation scenario of Psi and PF8

Based on the above experimental results, herein, we proposed a possible scenario of emerging CD-/CPL-active PF8 aggregate when CD-/CPL-silent PF8 was employed with PSI-S as a helix scaffold (Figure 9), as follows.

Stage I. In good solvents (toluene and chloroform), semi-flexible PF8 has a rich conformational freedom along C–C single bonds between fluorene rings, whereas PSI-S adopts a rigid 7₃-helical structure due to restricted rotation of Si–Si single bonds. Long n-hexyl and n-octyl side chains are fully interacted with solvents and should adopt a fairly stretch out geometry.

Stage II. By changing from pure good solvent to poorer cosolvent by employing a slow addition of methanol, PSI-S preferentially self-assembles to a higher-order helical structure, while PF8 exists as individual polymer chain even in the poorer cosolvent. The key factor is that PSI-S possesses an intense self-aggregation ability relative to PF8, arising from great differences in main chain rigidity and solubility in the solvent. In this case, n-hexyl groups should adopt a shrunk geometry.

Stage III. From the poorer to definitively poor cosolvents by further addition of methanol, the higher-order PSI-S helical motif causes a complexation with PF8 due to its limited solubility in the poor solvent. Multiple C-H/C interactions between n-hexyl groups of PSI-S and n-octyl groups of PF8 are responsible for the attractive macromolecular complexation. In this case, matching in side chain lengths of PSI-S and PF8 is another critical factor. Then, PSI-S helicity is efficiently transferred to PF8 due to a great loss of conformational freedom, yielding CD-/CPL-active, but metastable β-phase PF8 hetero-aggregate kept by rigid PSI-S helicity. The metastability
was confirmed by complete loss of CD signal of PF8 when chloroform was added to the hetero-aggregate.

Stage IV. The hetero-aggregate consisting of PSI-S and PF8 turns to CD-/CPL-PF8 aggregate after a complete removal of PSI-S as a helix scaffold by photoscissoring reaction at Sir-Sir* transition. In this case, PF8 chains turn into thermodynamically stable chiral β-phase. The chiral β-phase PF8 structures are stabilised through multiple C-H/C interactions between n-octyl groups.

4. Conclusion
In conclusion, we have reported the first photchemically controlled scaffolding of hetero-aggregates consisting of PSI and PF8 via a PSI-selective photoscissoring reaction. This protocol allowed for the successful production of a CPL- and CD-active PF8 aggregate by complete removal of PSI. Surprisingly, the hetero-aggregates may be a supermacromolecule consisting of two PSI chains and one PF8 chain. We assumed that sufficiently strong attractive C-H/C interactions existing between two n-octyl groups of PF8 and one n-hexyl group of PSI are responsible for scaffolding capability, regardless of the absence of electrostatic, hydrogen-bonding, dipole-dipole, CH/π/CH, CH/O and π/π interactions.

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6. Notes and references


An enantiopair of rigid rod-like helical polysilanes as a photoscissible scaffold allowed for the production of CPL- and CD-active diocetylpolyfluorene aggregates associated with complete removal by polysilane-selective photoscissoring reaction at 313 nm.