Synchronization in Non-Mirror-Symmetrical Chirogenesis: Non-Helical π-Conjugated Polymers with Helical Polysilane Copolymers in Co-Colloids

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Abstract: A curious question is whether two types of chiroptical amplifications, called sergeants-and-soldiers (Ser-Sol) and majority-rule (Maj) effects, between non-charged helical copolymers and non-charged, non-helical homopolymers occur when copolymer encounter homopolymer in co-colloids. To address these topics, the present study chose (i) two helical polysilane copolymers (HCPSs) carrying (S)- or (R)-2-methylbutyl with isobutyl groups as chiral/achiral co-pendants (type I) and (S)- and (R)-2-methylbutyl groups as chiral/chiral co-pendants (type II) and (ii) two blue luminescent π-conjugated polymers, poly[(dioctylfluorene)-alt-(trans-vinylene)] (PFV8) and poly[dioctylfluorene] (PF8). Analyses of circular dichroism (CD) and circularly polarized luminescence (CPL) spectral datasets of the co-colloids indicated noticeable, chiroptical inversion in the Ser-Sol effect of PFV8/PF8 with type I HCPS. PF8 with type II HCPS showed the anomalous Maj rule with chiroptical inversion though PFV8 with type II HCPS was the normal Maj effect. The noticeable non-mirror-symmetric CD-and-CPL characteristics and marked differences in hydrodynamic sizes of these colloids were assumed to originate from non-mirror-symmetrical main-chain stiffness of HCPSs in dilute toluene solution. The present chirality/helicity transfer experiments alongside of previous/recent publications reported by other workers and us allowed to raise the fundamental question; is mirror symmetry on macroscopic levels in the ground and photoexcited states rigorously conserved?

Keywords: circular dichroism; circularly polarized luminescence; sergeants-and-soldiers; majority-rule; polysilane; polyfluorenevinylenyl; polyfluorene; mirror symmetry breaking; parity violation

1. Introduction

Regarding the origin of life on Earth [1–14], in 1920s–1930s, Oparin [15] and Hal dane [16] proposed the coacervates hypothesis which states that the cell-wall free particles comprising organic constituents dispersed in water are a prototype of living cells during the chemical evolution of life. The coacervates are sphere-like colloids, ranging in size from 1 µm to 100 µm in diameter. Although the “macromolecule” hypothesis proposed in 1920s by Staudinger was still established in the 1930s, non-charged and charged colloids made of macromolecules (polymers) appear to not have been well-recognized in those days. In 1952, Terayama proposed the colloid titration method, in which oppositely charged polyelectrolytes allow for an instantaneous generation of polyelectrolyte complexes maintaining a neutrality of net charges by compensation between polycations and polyanions [17].

Supramolecular chirality induction means that mirror-symmetry-breaking (MSB) in achiral multiple molecular systems occurs upon non-covalent interactions through molecular chirality transfer scenarios. Since the times of Frederic Kipping in 1898 (NaClO3 with...
D-sugars) [18], Eligio Perucca in 1919 (triarylmethane dye with D-\(\text{NaClO}_3\) crystal) [19], and Paul Pfeiffer in 1932 (labile racemic \(\text{Zn}^{2+}, \text{Cd}^{2+}, \text{Ni}^{2+}\) complexes with \(L\)-amino acids) [20]. MSB phenomena have been widely observed in the realms of crystallography, artificial systems, and naturally occurring systems for over a century. In 2000 and 2004, Borovkov and Inoue coined the term chirogenesis to account for MSB phenomena observed for supramolecular chirality induction of achiral bisporphyrins endowed with several chiral amines and chiral alcohols in solutions [21,22]. MSB plays a key role in providing various chiroptical functionalities and sensing [21–24]. The generality of chirogenesis unifying attractive/repulsive intermolecular chirality transfer capability should be widely applicable to binary colloidal polymer systems upon non-covalent interactions by assorting multiple non-charged, less-polar polymers: e.g., (i) achiral polymer and chiral polymer, (ii) non-helical polymer and helical polymer, and, more in general (iii) optically inactive polymer and optically active polymer. Particularly, semi-flexible and rod-like chain-like polymers reveal marked cooperativity in response to external chemical and physical stimuli in dilute solutions, aggregates and in the condensed phase.

However, an intimate connection between classical/ modern optics and colloids was not fully understood until recently [25]; colloids work as \(\mu\text{-size}\) resonators that can boost chiroptical signals by several orders of magnitude. In macroscopic solid-state optics, mm-/cm-size ball and half-ball lenses are commonly used to efficiently collect incident light and focus emitted light into other devices. To significantly boost optical signals, one can obtain optical resonators and/or cavities by tailoring topologically designed devices like droplets, spheres, truncated spheroids, microdisks, and tori as a fusion of disk and sphere [26–30], enabling an efficient whispering-gallery mode (WGM) with extremely high quality (called \(Q\))-factors. The WGM principle covers a broad range of sound waves, guided surface waves, and various electromagnetic waves like radio, optics, Roentgen, and matter waves [26–37]. In 2006, a new concept in modern optics was coined—optofluidics—that combines microfluidics and solid-state optics [38–43]. Designing and fabricating \(\mu\text{-scale}\) liquid-based optical resonators is possible by: (i) tailoring the refractive index (RI) of the surrounding fluidic medium, (ii) making an optically smooth solid(liquid)-liquid interfaces without sub-\(\mu\text{-order}\) optical polishing, and (iii) confining mass-less photons in optical resonators having any topological shape, including liquid-core and/or liquid-clad optical waveguides [44,45].

The idea of fusion between neutral and charged colloids, coacervates, chirogenesis, WGM, and optofluidics prompted us to investigate chiroptical characteristics in the ground and photoexcited states of several \(\mu\text{-size}\) chromophoric and/or luminophoric colloidal polymers with high RIs, like helical/non-helical \(\sigma\)-conjugated dialkypolysilanes (\(\text{PSis}\)) and helical/non-helical \(\pi\)-conjugated dialkylpolyfluorene (\(\text{PF}\)) derivatives, with help of surrounding chiral-and-achiral fluidic medium with a tuned lower RI to maximize WGM effect [25]. These optofluidic colloidal polymers cause resonantly-enhanced chiroptical signals such as circular dichroism (CD), circularly polarized luminescence (CPL), and CPL excitation (CPLE) spectral signals. Ultraweak chiroptical signals, in which the degree of circular polarization \((g)\) is \(\sim 10^{-4} (5 \times 10^{-3}\%)\) from several \(\text{PSis}\) and \(\pi\)-conjugated polymers at the ground and photoexcited states in homogeneous solutions significantly boosted CD, CPL, and CPLE signals by three-to-five orders of magnitudes up to \(g \sim 0.7\) (35\%) when colloidal polymers are dispersed in the tuned RI optofluidic medium [25]. These results encouraged us to further design several \(\mu\text{-sized}\) co-colloids comprising helical/chiral dialkylpolysilane homopolymers (\(\text{HPSs}\)) and non-helical/achiral \(\pi\)-conjugated FL-based polymers as suspension state in the tuned RI optofluidic medium [25]. HPS had efficient helicity/chirality transfer capability to several FL-based polymers in the co-colloids. Furthermore, the enhanced CD and CPL signal amplitudes from several FL-based polymers led by HPS almost retained, even after a complete removal of HPS by an HPS-selective photoscissoring upon 313-nm irradiation for a short period [25].

Semiflexible/rod-like chain-like polymers, \(\pi\)-\(\pi\) stacked supramolecules, and aggregates are known to nonlinearly amplify their chiroptical signals in response to (S)-(R)-
chirality of internal building blocks and external chemical influences. Green was the first to report the sergeants-and-soldiers (Ser-Sol) and majority-rule (Maj) effects of chiroptical spectra using several semi-flexible polyisocyanate copolymers [46–48]. The Ser-Sol effect stands for the non-linear induction of non-racemic helical structures and chiral organizations endowed with a tiny amount of either chiral pendant chirality or external chiral guest [46]. The Maj-rule effect refers to the non-linear induction of non-racemic helical structures and/or chiral organizations led by enantiomerically impure pendant chirality and/or external chemical constituents [47]. Yashima and Maeda comprehensively demonstrated the Ser-Sol and Maj-rule effects in a series of single-strand poly(phenylacetylenes) and poly(diphenylacetylenes), and double-strand helical oligomers, that carrying (S)- or (R)-chiral and achiral pendants in the absence and presence of chiral and achiral guest molecules in solutions [49–54]. Nagata and Suginome investigated Ser-Sol and Maj-rule effects of poly(quinoxaline-2,3-diyl) derivatives bearing (S)/(R)-chiral and achiral pendant chirality [55–57]. Meijer, Palmans, and coworkers studied Ser-Sol and Maj-rule effects in supramolecular aggregates of substituted polythiophenes, substituted oligo(phenylenevinylene), and π−π stacks of three-fold symmetrical molecules [58–61]. To our view, several papers reported incomplete MSB phenomena (namely, one-side MSB) Ser-Sol effects in a series of only (S)/achiral co-pendants or (R)-/achiral co-pendants and one-side Maj effects in a series of only (S)- or (R)-rich co-pendants in the molecular and polymer systems. Previous reviews two decades ago reported preliminary results of both-side Ser-Sol and both-side Maj effects of polysilane copolymers with ultrahigh molecular weights (~10^6) in isooctane without noting any details [62,63]. A naive question that remains to us is whether the both-side Ser-Sol and Maj effects are rigorously mirror-symmetrical in inhomogeneous systems such as homo-colloids and co-colloids with π-conjugated polymers dispersed as a suspension in a fluidic medium.

Regarding the origin of biomolecular chirality on Earth, more naive questions are: (i) why are RNA, RNA, and proteins not simple polymer consisting of a single D-sugar and L-amino acid though they are regarded as well-designed random copolymers with controlled sequences, (ii) why RNA and DNA chose five-membered D-furanose, but not six-membered D-pyranose. A recent work showed that a very specific region of protein forms a supramolecular complex by recognizing and binding specific DNA [64]. It is widely known that RNA and DNA are unstable to deep-UV (so-called UV-C)/vacuum-UV (VUV) light which causes fatal damage to nucleobases and scissoring of C−C/C−O/C−N single bonds while proteins are considerably stable toward the UV light source [65]. If UV-C/VUV light is irradiated on a protein-DNA complex, DNA will preferentially degrade, but proteins might survive. Artificially designed co-colloids comprising photoscissable polysilane and non-photoscissable FL-polymers are suitable models of the protein-DNA complex [25,66,67].

By learning the noticeable Ser-Sol and Maj-rule effects in homogenous solutions and aggregates/coiloids as suspension in heterogeneous solutions [46–63], an apt question remains unanswered; whether the Ser-Sol and Maj effects between non-charged helical polysilane copolymers (HCPS) and non-charged, non-helical/achiral π-conjugated homopolymers occur when HCPS encounter FL-based homopolymers in the co-colloids in an RI-tuned, non-charged achiral optofluidic medium, enabling a WGM-driven chiroptical enhancement in their ground and photoexcited states.

The present work chose: (i) type I HCPS-S and -R bearing (S)- or (R)-2-methylbutyl and isobutyl groups as co-pendants, (ii) type II HCPS-SR substituted with (S)- and (R)-2-methylbutyl groups as co-pendants, and (iii) all-trans poly[(9,9-dioctylfluorene-2,7-vinylene)] (PFV8) [68–70] and poly(9,9-dioclylfluorene) (PF8) [67] as blue-color highly luminescent polymers by means of CD, CPL, and CPLE spectroscopy (Figure 1). HPS-S and -R, type I HCPS-S and -R, and type II HCPS-SR with lower molecular weight fractions of number-average molecular weight (M_n) = (5–11) × 10^4 and narrower polydispersity index (PDI) = 1.2–2.6 were used (see the Experimental section and Supplemental Information (SI), Tables S1–S3). The μm-size co-colloids comprising type I HCPS and PFV8/PF8...
revealed noticeable Ser-Sol effects associated with chiroptical inversion at specific mole fractions of the chiral pendant. Likewise, the Maj effect of type II HCPS with PFV8/PF8 in the µm-size co-colloids was obvious. These Ser-Sol and Maj effects in the co-colloids were synchronized with those from the homo-colloids of types I/II HCPSs. The CD-/CPL-active PFV8/PF8 endowed with types I/II HCPSs in the co-colloids afforded the corresponding CD-/CPL-active PFV8 and PF8 homo-colloids by removing HCPSs by the 313-nm Si–Si bond selective photoscissoring reaction.

Figure 1. Chemical structures of poly[(9,9-di-n-octylfluorene)-alt-(trans-vinylene)] (PFV8), poly(di-n-octylfluorene) (PF8), poly(n-hexyl-(S)-2-methylbutylsilane (HPS-S), poly(n-hexyl-(R)-2-methylbutylsilane (HPS-R), poly(n-hexyl-(S)-2-methylbutylsilane)-co-(n-hexyl-isobutylsilane) (type I HCPS-S), poly(n-hexyl-(R)-2-methylbutylsilane)-co-(n-hexyl-isobutylsilane) (type I HCPS-R), and poly(n-hexyl-(S)-2-methylbutylsilane)-co-(n-hexyl-(R)-2-methylbutylsilane) (type II HCPS-SR).

2. Results
2.1. Sergeants-and-Soldiers and Majority-Rule of Type I HCPS and Type II HCPS
2.1.1. Sergeants-and-Soldiers of Type I HCPS-S and -R in Isooctane and Homo-Colloids in CHCl3-MeOH Cosolvents

First, Figure 2a,b show the monosignate, extremely narrow CD along with extremely narrow UV spectra (full-width-at-half-maximum; 8 nm) at 320–323 nm of type I HCPS-S (x = 1.00, 0.10, 0.05, and 0.006) and type I HCPS-R (x = 1.00, 0.10, 0.05, and 0.007) dissolved in a dilute homogeneous isooctane solution ([conc] = 2 × 10^{-4} M (pathlength 10 mm) at −5 °C, respectively. Clearly, CD and UV spectral profiles of type I HCPS-S copolymers are almost identical to those of HPS-S (type I HCPS-S, x = 1.00). Likewise, CD and UV spectral profiles of type I HCPS-R copolymers are almost identical to those of those of HPS-R (type I HCPS-R, x = 1.00). These CD and UV spectra and the Ser-Sol characteristics of lower molecular weight (Mn = (5–11) × 10^4) type I HCPS-S and -R are almost identical to those of the high molecular weight (type I HCPS-S and -R [62,63]. These unique CD-UV bands are characteristic of quasi-one-dimensional exciton (e-h pair) confined into rod-like 73-helical dialkylpolysilanes with 0.5-nm width quantum wire [71].
Figure 2. (a) The representative monosignate CD and UV spectra of medium molecular weight \((M_n = (2–4) \times 10^4)\) type I HCPS-S \((x = 1.00 \text{ (black lines)}, 0.10 \text{ (green lines)}, 0.05 \text{ (blue lines)}, \text{ and } 0.006 \text{ (red lines)})\) in a dilute isooctane solution \([\text{conc as Si–Si repeating unit} = 2 \times 10^{-4} \text{ M (pathlength 10 mm) at } -5 \degree \text{C}].\) (b) The representative monosignate CD and UV spectra of type I HCPS-R \((x = 1.00 \text{ (black lines)}, 0.10 \text{ (green lines)}, 0.05 \text{ (blue lines)}, \text{ and } 0.007 \text{ (red lines)})\) in a dilute isooctane solution \([\text{conc} = 2 \times 10^{-4} \text{ M (pathlength 10 mm) at } -5 \degree \text{C}].\) (c) The bisignate couplet-like CD and UV spectra of type I HCPS-S homo-colloids \((x = 1.00, 0.50, 0.25, 0.10, 0.05, 0.02, \text{ and } 0.006)\) and -R \((x = 1.00, 0.50, 0.25, 0.10, 0.05, 0.02, \text{ and } 0.007)\) in CHCl3/MeOH = 2.0/1.0 \((v/v)\). (d) A comparison of the normal and anormal sergeants-and-soldiers effects in cooperative chiroptical enhancement; the \(g_{\text{CD}}\) at the first Cotton band (CD extremum: \(\lambda_{\text{ext}}\)) vs. mole fractions of the \((S)-(R)\) pendant chirality in the non-colloidal type I HCPS-S and -R in isooctane at \(-5 \degree \text{C} (\text{red filled circles})\) and the homo-colloidal suspension at 25 °C in the cosolvent (blue filled circles). The \(g_{\text{CD}}\) values of non-colloidal HPS-S and -R \((\text{red filled circles})\) were taken from Figure 2a,b. The \(g_{\text{CD}}\) values of ultrahigh molecular weight \((\sim 10^6)\) HPS-S and -R, and HCPS-S and -R \((\text{red crosses})\) were adopted from the original datasets [62,63]. (e) Zoom-in plots of Figure 2d. (f) A comparison of the \(g_{\text{CD}}\) values at the first Cotton \((320–326 \text{ nm, right ordinate, blue circles})\) and second Cotton \((308–312 \text{ nm, left ordinate, red circles})\) bands vs. mole fraction of the \((S)-(R)\) pendant chirality in type I HCPS-S and -R homo-colloids in the cosolvent at 25 °C. (g) Zoom-in plots of Figure 2f. (h) A comparison of two CD extrema \(\lambda_{\text{ext}}\) at the first Cotton band (right ordinate, blue circle) and the second Cotton band (left ordinate, red circle) vs. mole fractions of the \((S)-(R)\) in type I HCPS-S and -R homo-colloids.
Figure 3. (a) The monosignate CD and UV spectra of lower molecular weight (M_n = (2–4) × 10^4) type II HCPS-SR [(S)/(R) = 1.00/0.00 (thin blue lines) and 0.53/0.47 (thick blue lines)] in a dilute isooctane solution ([conc as Si-Si repeating unit] = 2 × 10^{-4} M (pathlength 10 mm) at −5 °C. (b) The monosignate CD and UV spectra of type II HCPS-SR [(S)/(R) = 0.00/1.00 (thin red lines) and 0.47/0.53 (thick red lines)] in the dilute isooctane at −5 °C. (c) The changes in bisignate couplet-like CD and UV spectra of type II HCPS-SR [(S)/(R) = 1.00/0.00, 0.60/0.40, 0.53/0.47, 0.50/0.50, 0.47/0.53, 0.40/0.60, 0.00/1.00] homo-colloids in CHCl_3/MeOH = 2.0/1.0 (v/v) vs. (d) A comparison of the majority effects in cooperative chiroptical enhancement; the g_{CD} value (red filled circles) at ~323 nm of type II HCPS-SR in isooctane at −5 °C and the g_{CD} values (blue filled circles) with λ_{ext} values (as insets) at the first Cotton band of the colloids in the co-solvent at 25 °C vs. mole fractions of the (S)-(R) chirality. The g_{CD} values of ultrahigh molecular weight (~10^6) HCPS-S and -R (red crosses) were adopted from the original datasets [62,63]. For visibility, (−)- and (+)-numerical data in a right-side ordinate flips upside down.

Figure 2c shows the CD and UV spectra of type I HCPS-S (x = 0.006–1.00) and -R (x = 0.007–1.00) homo-colloids vs. mole fractions of the (S)-(R). It is clear that drastic changes in spectral shape from mono- to bisignate couplet-like CD spectra characteristics of aggregates [25,72], herein, called homo-colloids, of helical polysilane homo- and copolymers dispersed in poor–good cosolvents. The changes in chiroptical spectra are similar to those of rod-like helical polysilane homopolymers carrying longer n-decyl/n-dodecyl and (S)/(R)-2-methylbutyl achiral/chiral co-pendants [25,72].

Figure 2d,e compares the g_{CD} values vs. mole fractions of the (S)-(R) in the type I HCPS-S and -R as non-colloid (red filled circles) and homo-colloids (blue filled circles), associated with the λ_{ext} value at the first Cotton band (320–326 nm) of the colloids. The relation of the g_{CD} value–mole fractions of the (S)-(R) in the non-colloidal copolymers shows a normal-type Ser-Sol effect; a small fraction of the pendant chirality, ~10 mol %, in the copolymers induces nearly identical helical structures of HPS-S and -R homopolymers. The Ser-Sol effect of lower molecular weight HPS and type I HCPS (red filled circles) are almost identical to that of ultrahigh molecular weight (~10^6) ones (red crosses) [62,63]. Contrary, the relation of the g_{CD} value–mole fractions of the (S)-(R) in the colloidal copolymers shows anomaly in the Ser-Sol effects; apparent chiroptical sign inversion occurs between 25 mol % and 50 mol % of the pendant chirality disregard of (S) and (R). In the fraction of the pendant
chirality ranging from 0.006 (S) or 0.007 (R) mol % to 25 mol % of the (S)-(R), the $\xi_{CD}$ value tends to increase with the mole fractions of the (S)-(R) associated with some fluctuation behavior. The chiroptical inversion in the Ser-Sol type I HCPS-$S$/-$R$ homo-colloids are transferred to PFV8/PF co-colloids with type I HCPS-$S$/-$R$, discussed later sections.

Figure 2f,g plots the $\xi_{CD}$ values at the first and second Cotton bands (\(\lambda_{ext}\)) vs. mole fractions of the (S)-(R) in type I HCPS-$S$ and type I HCPS-$R$ homo-colloids in CHCl$_3$/MeOH = 2.0/1.0 (v/v) at 25 °C. The CD sign inversion occurs between 25 and 50 mol % fractions of the pendant chirality regardless of the $S$-$R$. The absolute $\xi_{CD}$ values, $|\xi_{CD}|$, vs. mole fractions of the (S)-(R) are not mirror-symmetrical. The $|\xi_{CD}|$ values of type I HCPS-$S$ (\(x = 1.00, 0.50, 0.25\)) are large twice compared to those of type I HCPS-$R$ (\(x = 1.00, 0.50, 0.25\)).

Figure 2h depicts the $\lambda_{ext}$ values at the first and second Cotton bands vs. mole fractions of the (S)-(R) in type I HCPS-$S$ and type I HCPS-$R$ homo-colloids. The relation of the $\lambda_{ext}$ – (S)-(R) mol fraction is not mirror-symmetrical regardless of the first and second Cotton bands. The anomalous CD inversion, non-mirror-symmetrical Ser-Sol effect in type I HCPS homo-colloids is transferred to similar anomalous CD inversion, non-mirror-symmetrical CD characteristics in PFV8/PF8 co-colloids with type I HCPS-$S$ and type I HCPS-$R$ discussed in later sections.

2.1.2. Majority-Rule of Type II HCPS in Isooctane and Homo-Colloids in CHCl$_3$-MeOH Cosolvents

Figure 3a,b show the similar extremely narrow CD and extremely narrow UV spectra of type II HCPS-SR (\(S/R = 1.00/0.00\) (red line) and 0.53/0.47 (blue line)) and type II HCPS-SR [(S)/(R) = 0.00/1.00 (red line) and 0.47/0.53 (blue line)] in a dilute isooctane solution at $-5 \degree$C, respectively. Clearly, CD and UV spectral profiles of type II HCPS-SR copolymer [(S)/(R) = 0.53/0.47] are almost identical to those of HPS-$S$. Likewise, CD and UV spectral profiles of type II HCPS-SR copolymer [(S)/(R) = 0.47/0.53] are almost identical to those of HPS-$R$. These CD-UV spectra and Maj characteristics of lower molecular weight type II HCPS-SR (\(M_n = (2-4) \times 10^4\)) are almost identical to those of ultrahigh molecular weight (\(M_n = (1-8) \times 10^6\)) type II HCPS-SR [69,70].

Figure 3c shows the CD and UV spectra of type II HCPS-SR homo-colloids as a function of mole fraction of chiral pendants [(S)/(R) = 1.00/0.00, 0.60/0.40, 0.53/0.47, 0.50/0.50, 0.47/0.53, 0.40/0.60, 0.00/1.00] in the chiral/chiral co-pendants in CHCl$_3$/MeOH = 2.0/1.0 (v/v) cosolvents. Likewise, the changes in spectral shape from monosignate to bisignate couplet-like CD spectra are characteristics of homo-colloidal helical polysilane hom- and copolymers in poor-good cosolvents with the tuned \(n_D = 1.407\).

The CD profiles of type II HCPS (red filled circles) are almost identical to that of ultrahigh molecular weight (\(\sim 10^6\)) ones (red crosses) [62,63]. Similarly, the $\xi_{CD}$ value–mole fractions of the (S)-(R) in the non-colloidal copolymers shows a clear normal Maj-type cooperativity; $\sim 20$ mol %ee of the (S)-(R) pendant chirality in the copolymers induces nearly identical to helical homopolymers with 100 mol % pure (S)- and (R)-chirality. This Maj effect of lower molecular weight HPS and type II HCPS (red filled circles) are almost identical to that of ultrahigh molecular weight (\(\sim 10^6\)) ones (red crosses) [62,63]. Similarly, the $\xi_{CD}$ value–mole fractions of the (S)-(R) in the non-colloidal copolymers shows a clear normal Maj-type cooperativity; $\sim 20$ mol %ee of the (S)-(R) pendant chirality in the copolymers induces nearly identical helical structure of HPS-$S$ and -$R$ homo-colloids with pure (S)- and (R)-chirality. The $|\xi_{CD}|$ values vs. mole fractions of the (S)-(R)-chirality, however, are not mirror-symmetrical. The $|\xi_{CD}|$ values of (S)-rich type II HCPS-SR [(S)/(R) = 0.60/0.40, 0.53/0.47] are large twice compared to those of (R)-rich one [(S)/(R) = 0.40/0.60 and 0.47/0.53]. The non-mirror-symmetrical Maj effect in type II HCPS-SR homo-colloids are transferred to non-mirror-symmetrical Maj effects in the co-colloids with PFV8 and PF8 discussed in later sections.

2.2. Sergeants-and-Soldiers in PFV8 Co-Colloids with Type I HCPS-$S$ and -$R$

Based on the several parameters optimized experimentally, the CD and UV-visible spectra of PFV8 co-colloids with HPS-$S$ and -$R$ (1:1 in mole ratio) generated at the opti-
mized nD of CHCl3/MeOH = 2.0/1.0 (v/v) are given in Figure 4a (see, Experimental section and SI, Figure S40). Clearly, PFV8 emerges the bisignate couplet-like CD spectra in the range of 350 nm and 500 nm, that are ascribed to several π–π* bands of PFV8 backbone. Main-chain helicity and/or pendant chirality of HPS-S induce (−)-sign vibronic CD bands at 468.0 nm and 435.5 nm with a spacing of 1594 cm⁻¹ at π–π* transitions of PFV8 backbone. The 1594-cm⁻¹ spacing is related to aromatic ring and/or vinylic C=C stretching vibrations. Also, one can be aware of a weaker, broader (+)-sign CD band around 400 nm. Conversely, HPS-R induce (+)-sign vibronic CD bands at 465.5 nm and 434.0 nm with a 1562 cm⁻¹ spacing associated with a weak, broad (−)-sign CD band around 400 nm. HPS-S and -R provide nearly mirror-symmetrical couplet-like CD spectral profiles in the range of 350 nm and 500 nm though the absolute magnitudes of $\delta_{CD}$ values, $\delta_{CD}$, at these bands are unequal and not mirror-symmetrical. It is obscure of which chirality of HPS, Si–Si main-chain helicity and pendant chirality is a deterministic factor for emerging the CD-active PFV8 in the co-colloids. Both helicity and pendant chirality are assumed to contribute collaboratively and non-collaboratively for the generation of CD-active PFV8.

Next, Figure 4b shows the progressive changes in the couplet-like CD associated with UV-visible spectra of PFV8 co-colloids with type I HCPS-S and -R varying mole fractions of the (S)-(R). For clarity, Figure 4c shows their zoom-in CD and UV-visible spectra of the PFV8 co-colloids to highlight the chiroptical properties of PFV8. Likewise, the changes in monosignate CD spectral shape to bisignate couplet-like one associated with characteristics of type I HCPS homo-colloids is obvious.

Figure 4d,e plot the $\delta_{CD}$ values at 325 nm of type I HCPS (blue circles) and at ~460 nm of PFV8 (red circles), respectively, vs. mole fractions of the (S)-(R). Obviously, the $\delta_{CD}$ characteristics of PFV8 in the co-colloids are similar to those of type I HCPS in the co-colloids. The relation between the $\delta_{CD}$ values (PFV8) and mole fractions of the (S)-(R) shows the similar anomaly in the Ser-Sol effects of type I HCPS homo-colloids (Figure 2d,e); an apparent CD sign inversion occurs between 25 mol % and 50 mol % mole fractions of the (S)-(R). The CD signal characteristics of PFV8 endowed with type I HCPS and HPS are synchronized with the nature of main-chain helicity and/or pendant chirality of type I HCPS and HPS.

From Figure 4f, PFV8 unexpectedly reveals bisignate, vibronic CPL spectral bands excited at 350 nm; (+)-CPL at 480.0 nm and 502.0 nm associated with (−)-CPL at 464.0 nm on application of HCPS-S (x = 0.10) and (−)-CPL at 479.5 nm and 508.0 nm associated with (+)-CPL at 460.5 nm on application of HCPS-R (x = 0.10). For comparison, PFV8 reveals the opposite bisignate, vibronic CPL spectra excited at 350 nm when HPS-S and -R are employed; (+)-CPL at 480.0 nm and 502.0 nm associated with (−)-CPL at 464.0 nm on application of HPS-S and (−)-CPL at 482.0 nm and 504.5 nm associated with (+)-CPL at 464.0 nm on application of HPS-R. The chiroptical inversion in CPL spectra is directly connected to that in CD spectral characteristics.

The CPLE spectra of PFV8 by monitoring both (+) and (−)-CPL signals allow to verify the origin of the bisignate CPL spectra (Figure 4g,h). This technique are applied to optically active colloidal polymers and molecular (1S)-(−)/(1R)-(+) camphor that reveal bisignate CPL bands [25]. Type I HCPS-S (x = 0.10) revealed the bisignate CPLE spectral characteristics. A broad (+)-CPLE band (blue line) at 450 nm is detected in the range of 300 nm and 470 nm by monitoring at 500 nm of CPL band, conversely, a broad (−)-CPLE band (red line) in the range of 300 nm and 420 nm is evident by monitoring CPL band at 480 nm. Likewise, a broad (−)-CPLE bands (blue and green lines) at 420–450 nm in the range of 300 nm and 470 nm is seen by monitoring CPL bands at 480 nm and 500 nm, conversely, a broad (+)-CPLE spectrum (red line) in the range of 300 nm and 430 nm can be seen by monitoring CPL band at 462 nm. From the bisignate CPLE characteristics, PFV8 main-chain in the co-colloid revealing the bisignate CPL signals excited at 350 nm originates from the bisignate couplet-like CD bands (~400 nm/~420 nm and ~460 nm). Twisting stacking structures of PFV8 are responsible for the couplet-like CD bands. These CPLE and PLE spectroscopic datasets led to conclude that type I HCPS-S and -R do not
contribute directly to these CPL and PL spectra in the 350 nm and 500 nm because of no CPL and PL spectra characteristic of the Si–Si backbone ranging from 250 nm and 350 nm.

**Figure 4.** (a) The CD and UV-visible spectra of PFV8 co-colloids with HPS-S (blue lines) and -R (red lines) (1:1 mole ratio) in CHCl<sub>3</sub>/MeOH = 2.0/1.0 (v/v). (b) The changes in the CD and UV-visible spectra of PFV8 co-colloids with type I HCPS-S homo-colloids (x = 1.00, 0.50, 0.25, 0.10, 0.05, 0.02, and 0.006) and -R (x = 1.00, 0.50, 0.25, 0.10, 0.05, 0.02, and 0.007) (1:1 mole ratio) in the co-solvent at 25 °C and (c) the corresponding zoom-in spectra of PFV8 co-colloids. (d) The $\gamma_{\text{CD}}$ values of PFV8 at 460–468 nm (right ordinate, filled circles) and type I HCPS-S and -R at 320–324 nm (left ordinate, red circles) vs. mole fractions of the (S)-(R). (e) Zoom-in plot of Figure 4d. (f) The inversion CPL associated with the corresponding PL spectra excited at 350 nm of PFV8 co-colloids with HPS-S (thin blue lines) and -R (thin red lines) and type I HCPS-S (x = 0.10, thick blue lines) and -R (x = 0.10, thick red lines) in the co-solvent. (g) The CPLE and PLE spectra monitored at 465 nm (red lines) and 500 nm (blue lines) of PFV8 co-colloids with type I HCPS-S (x = 0.10) in the co-solvent. (h) The CPLE and PLE spectra monitored at 462 nm (red lines), 480 nm (blue lines), and 510 nm (green lines) of type I HCPS-R (x = 0.10) in the co-solvent.
Yet, it remains obscure which the main-chain helicity or pendant chirality is responsible for the CD/CPL inducibility to PFV8. **Type I HCPS** is assumed to non-covalently interact with PFV8, allowing for generating helical/chiral organizations that emerge CPL and CD signals characteristic at $\pi-\pi^*$ transitions of PFV8.

### 2.3. Majority-Rule in PFV8 Co-Colloids with Type II HCPS

The synchronized Ser-Sol characteristics of PFV8 co-colloids endowed with **type I HCPS**-$S$ and -$R$ prompted us to further investigate the Maj characteristics of PFV8 co-colloids with **type II HCPS**-$SR$. Figure 5a displays the CD and UV-visible spectra of PFV8 co-colloids with **type II HCPS**-$SR$ (1:1 in mole ratio) generated at the same optimized $n_D$ of the CHCl$_3$/MeOH = 2.0/1.0 (v/v). Clearly, PFV8 emerges the bisignate couplet-like CD spectra in the range of 350 nm and 500 nm, ascribed to several $\pi-\pi^*$ transitions of PFV8. Main-chain helicity and/or pendant chirality of **type II HCPS**-$SR$ can induce (+)-sign vibronic CD bands at 468.0 nm and 435.5 nm with a spacing of 1410 cm$^{-1}$ at the corresponding $\pi-\pi^*$ transitions of PFV8 associated with a weaker, broader (-)-CD band at $\sim$ 390 nm when a fraction of (S)-chirality is over (R)-one. The 1410-cm$^{-1}$ spacing is related to aromatic ring and/or vinylic C=C stretching vibrations. Likewise, **HPS**-$R$ induces (-)-vibronic CD bands at 467.0 nm and 437.0 nm with a 1470 cm$^{-1}$ spacing associated with a weaker, broader (+)-CD band at $\sim$390 nm when a mole fraction of (R)-chirality is excess over (S)-one. Either the main-chain helicity or excess chirality in the pendants and/or both collaboratively contribute to generate the CD active PFV8.

![Figure 5](image-url)

**Figure 5.** (a) The changes in the CD and UV-visible spectra of PFV8 co-colloids with **type II HCPS**-$SR$ [(S)/(R) = 1.00/0.00, 0.60/0.40, 0.53/0.47, 0.50/0.50, 0.47/0.53, 0.40/0.60, 0.00/1.00] (1:1 mole ratio) vs. mole fractions of the (S)-(R) at 25 °C in CHCl$_3$/MeOH = 2.0/1.0 (v/v). (b) The corresponding $g_{CD}$ values at 322–325 nm for **type II HCPS**-$SR$ (left ordinate, red circles) and at 464–468 nm for PFV8 (right ordinate, blue circles), respectively, mole fractions of the (S)-(R). (c) The changes in the CPL and PL spectra excited at 350 nm of PFV8 co-colloids with **type II HCPS**-$SR$ (1:1 mole ratio) in the co-solvent. (d) The corresponding $g_{CPL}$ value at 474–483 nm of PFV8 co-colloids (right ordinate, blue circles) and the $g_{CD}$ value at 322–325 nm of **type II HCPS** (left ordinate, red circles) in the co-colloids, respectively, vs. mole fractions of the (S)-(R).

Figure 5b plots the $g_{CD}$ values at $\sim$460 nm of PFV8 (blue circles) and at 325 nm of **type II HCPS**-$RS$ (red circles), respectively, in the co-colloids as a function of mole fraction of the (S)-(R). It is obvious that a weak non-linear Maj effect of PFV8 is synchronized with the weak non-linear Maj effect of **type II HCPS**-$RS$ in the co-colloids. These non-linear Maj effects in the co-colloids is almost similar to those of **type II HCPS** homo-co-colloids (Figure 3d). The Maj-rule of PFV8 is synchronized with those of **type II HCPS**-$RS$. An ee
of the (S)-(R) pendant chirality cooperativity determines the CD characteristics of PFV8 and type II HCPS-RS in the co-colloids.

Figure 5c displays the changes in the CPL spectra associated with the corresponding PL spectra excited at 350 nm of the co-colloids vs. mole fractions of the (S)-(R). The absolute magnitude in the couplet-like CPL bands at ~460 nm and ~480 nm increases when the relative mole fractions of the (S)-(R) increases or decreases.

Figure 5d plots the $g_{\text{CPL}}$ values at 460 nm of PFV8 (blue circles) in the co-colloids and the $g_{\text{CD}}$ value at 325 nm of type II HCPS-RS (red circles) vs. the mole fractions of the (S)-(R). The Maj-rule of the $g_{\text{CPL}}$ (PFV8) vs. mole fractions of the (S)-(R) is similar to that of type II HCPS-RS in the co-colloids. The absolute magnitudes of $g_{\text{CPL}}$ and $|g_{\text{CPL}}|$ of PFV8 between $(R)/(S) = 1.00/0.00$ and $0.00/1.00$ and between $(R)/(S) = 0.60/0.40$ and $0.40/0.60$ significantly differ from each other. The $g_{\text{CPL}}$ values tend to shift largely toward (−)-values in all the (S)-(R).

The main-chain helicity and/or pendant chirality of type II HCPS-RS are non-covalently interacted with PFV8 in the co-colloids, allowing for generating chiral and/or helical structures responsible for these CPL and CD signals characteristic at $\pi-\pi^*$ transitions of PFV8. Noticeable non-mirror-symmetrical Maj effects in the ground and photoexcited states of PFV8 co-colloids with type II HCPS-RS are obvious.

2.4. Retention in CD and CPL Signals of PFV8 Co-Colloids with Type I HCPS and Type II HCPS by Si–Si Bond Selective Photolysis

A question remains unanswered whether CD and CPL signals of PFV8 with types I HCPS-S and -R disappear or are retained when the HCPSs are completely taken away from the co-colloids.

In the previous paper, the 313-nm photolysis allows for the efficient Si–Si bond selective scissoring of HPS-S and -R in the co-colloids with several $\pi$-conjugated polymers [25,67]; the resulting CD and CPL spectral magnitudes of the $\pi$-conjugated polymers almost retained after a complete removal of HPS-S and -R by the 313-nm photolysis [25,67]; any decomposition and alteration of PFV8 and PF8 did not occur. The 313-nm Si–Si bond selective photolysis offered the CD-/CPL-active PFV8 homo-colloids from PFV8 co-colloids with types I/II HCPSs.

Figure 6a,b depicts the CD and UV-visible spectra of PFV8 co-colloid with HPS-S and -R before and after irradiation of the 313-nm light source (20 $\mu$W cm$^{-2}$ for 10 s) in the 1-cm pathlength quartz cuvette under a gentle stirring with a magnetic stir bar. Clearly, after the 313-nm irradiation, the CD and UV-visible signals of PFV8 generated by HPS-S considerably retains, conversely, the CD signals of PFV8 endowed with HPS-R significantly diminish though UV-visible spectra are nearly unchanged. Although CD and UV bands in the range of 280 and 330 nm due to Si–Si bonds of HPS-S and -R completely disappeared, the scaffolding capability of HPS-S is efficient, but HPS-R appears inefficient.

Figure 6c compares the CPL and PL spectra excited at 350 nm of PFV8 co-colloid with HPS-S before and after the 313-nm photolysis (20 $\mu$W cm$^{-2}$ for 10 s). The CPL and PL signals of PFV8 considerably retains even after the photolysis. Figure 6d shows the changes in the CPL and PL spectra excited at 350 nm of the PFV8 co-colloids with type I HCPS-S (x = 0.10) and -R (x = 0.10) before and after the 313-nm photolysis. Disregard of the (S)-(R), the absolute CPL magnitudes of PFV8 diminishes by one-third upon the photolysis. On the other hand, from Figure 6e, the degree of changes in CPL and PL spectra of PFV8 co-colloids with type II HCPS-SR [(R)/(S) = 0.60/0.40 and 0.40/0.60] is nearly unchanged regardless of the (S)-(R).
Figure 6. (a) The change in the CD and UV-visible spectra of PFV8 co-colloids with HPS-S (1:1 mole ratio) before (thin blue lines) and after (thick blue lines) the 313-nm photolysis in CHCl₃/MeOH = 2.0/1.0. (b) The change in the CD and UV-visible spectra of PFV8 co-colloids with HPS-R (1:1 mole ratio) before (thin red lines) and after (thick red lines) the 313-nm photolysis in the co-solvent. (c) The changes in the CPL and PL spectra excited at 350 nm of PFV8 co-colloids with HPS-S (1:1 mole ratio) before (thin blue lines) and after (thick blue lines) the 313-nm photolysis. (d) The changes in the CPL and PL spectra excited at 350 nm of PFV8 co-colloids with type I HCPS-S (S = 0.10, blue lines) and -R (R = 0.10, red lines) (1:1 mole ratio) before (thin lines) and after (thick lines) the 313 nm photolysis. (e) The changes in the CPL and PL spectra of PFV8 co-colloids with type II HCPS-SR [(S)/(R) = 0.40/0.60 (red lines) and 0.60/0.40 (blue lines)] before (thin lines) and after (thick lines) the 313-nm photolysis.

The particle diameter ($D_H$) of the co-colloids as a suspension state may teach us the changes in the colloidal sizes before and after the 313-nm photolysis. According to dynamic light scattering (DLS) measurements and analysis before the 313-nm photolysis, the $D_H$ value of PFV8-HPS-S co-colloids in CHCl₃/MeOH = 2.0/1.0 (v/v) ranges from 288 nm and 513 nm, suggesting they maintain an almost constant value which fluctuates weakly with time (SI, Figure S32). On the other hand, the $D_H$ value of PFV8-HPS-R co-colloids ranges from 2924 nm and 4277 nm, that is larger by the one-order of magnitude compared to those of the PFV8-HPS-S co-colloids while maintaining these sizes with time (SI, Figure S34). For comparison, the $D_H$ value of PFV8-HCPS-SR [(S)/(R) = 0.50/0.50] co-colloids ranges from 539 nm and 735 nm (SI, Figure S36), close to that of PFV8-HPS-S co-colloids.

After the 313-nm photolysis, the $D_H$ value of the PFV8-HPS-S co-colloids ranges from 513 nm and 1160 nm and tends to increase by several fold while fluctuating with time (SI, Figure S33). The marked increase in the $D_H$ value may be ascribed to Ostwald ripening [73,74]. On the other hand, the $D_H$ value of the PFV-HPS-R co-colloid, ranging from 1709 nm and 2236 nm (513 nm is exceptional), considerably decrease after the 313-nm
photolysis while the $D_H$ values are weakly fluctuating with time (SI, Figure S35). The decrease in the $D_H$ value may arise from a reverse Ostwald ripening [75–77].

A further statistical analysis of these $D_H$ values (n = 10 measurements) (SI, Figures S32–S35) suggests that: (i) before the 313-nm photolysis, for PFV8 with HPS-S, $D_H = 321$ nm ± 22 nm (standard error (SE)), for PFV8 with HPS-R, $D_H = 3629$ nm ± 137 nm (SE), and for PFV8 with HCPS-SR, $D_H = 615$ nm ± 18 nm (SE); (ii) after the photolysis, for PFV8 with HPS-S, $D_H = 907$ nm ± 68 nm (SE) and for PFV8 with HPS-R, $D_H = 304$ nm ± 24 nm (SE). Before the photolysis, the mean size of PFV8 co-colloids with HPS-R is larger by approximately 11.3 times compared to that of PFV8 co-colloids with HPS-S. The relative ratio in the $D_H$ values of PFV8/HPS-R to PFV8/HPS-S corresponds to ~1440 by a volume ratio. Conversely, after the photolysis, the mean sizes of the former decreases by one-thirds relative to the latter, meaning that a relative volume ratio of PFV8 homo-colloid led by HPS-R to PFV8 homo-colloid led by HPS-S becomes small by ~27 times.

The noticeable differences in the $D_H$ values and relative volume ratio between the (S)-(R) may be connected to the significant differences in the viscosity index, $\alpha$, of non-colloids between the (S)-(R) in dilute toluene and the non-mirror-symmetrical CD and CPL spectral characteristics of PFV8 co-colloids with types I/II HCPSs between the (S)-(R) pendant chirality. A series of the 313-nm photolysis experiments of PFV8 co-colloids with HPS-S, -R, type I HCPS-S and -R, and type II HCPS-RS led to propose that the mole fractions of the (S)-(R) appear crucial rather than Si–Si main-chain helicity to induce CD-/CPL-activity in PFV8 in the co-colloids.

2.5. Sergeants-and-Soldiers in PF8 Co-Colloids with Type I HCPS

After optimizing the several parameters experimentally by choosing poor and good solvents [67], the changes in CD and UV-visible spectra of PF8 co-colloids with HPS-S and -R (1:2 in mole ratio) generated at MeOH-toluene cosolvent (1.5/1.5 (v/v)) with the tuned $n_D = 1.415$ were discussed.

From Figure 7a, HPS-S and -R in the PF8 co-colloids clearly reveal bisignate, couplet-like CD signals at the Siσ-Siσ* transitions, similar to the HPS-S and -R co-colloids with PFV8, and the HPS-S and -R homo-colloids. From Figure 7b, PF8 co-colloids with HPS-S and -R clearly reveal multiple couplet-like CD signals in the range of 350 nm and 450 nm, originating from different π-π stacks, β-phase (~430 nm) and α-phase (~400 nm), of PF8, [67,78–80]. These results prompted to measure the CD and UV-visible spectra of PF8 co-colloids with type I HCPS-S and -R (1:2 in mole ratio) at the same MeOH-toluene cosolvents (1.5/1.5 (v/v)) (Figure 7c).

Figure 7c–e highlight the changes in CD and UV-visible spectra of PF8 co-colloids with type I HCPS-S and -R, respectively, varying mole fractions of the (S)-(R). Clearly, the CD magnitudes and their CD signs of PF8 largely depend on the mole fractions of the (S)-(R). Their CD spectral characteristics of type I HCPS-S and -R in the co-colloids are almost identical to those of PF8 co-colloids with type I HCPS-S and -R homo-colloids.

Figure 7f,g displays the $g_{CD}$ values at 399–401 nm (α-phase) of PF8 and at 320–322 nm (the first Cotton band) of type I HCPS in the co-colloids as a function of mole fraction of the (S)-(R). We note that the $|g_{CD}|$ values between PF8 and type I HCPS in the co-colloids are very different (by one-order of the magnitude). A relation of the $g_{CD}$ (PF8)–mole fraction of the (S)-(R) is almost similar to that of $g_{CD}$ (type I HCPS)–mole fraction of the (S)-(R). The mole fractions of the (S)-(R) in type I HCPS are intimately connected to generation of the CD-active PF8. Likewise, the anormal Ser-Sol effects in the relation of $g_{CD}$ (PF8)–mole fraction of the (S)-(R) is evident. The chiroptical sign inversion in the $g_{CD}$ value of PF8 occurs at (S) ~ 50 mol % and (R) ~ 50 mol % though the $|g_{CD}|$ value at (R) = 50 mol % largely diminishes. The anormal Ser-Sol effects with sign inversion and marked non-mirror-symmetry in the relation of $g_{CD}$ (PFV8)–mole fraction of the (S)-(R) are obvious.

Figure 7h shows the comparisons of the CPL and PL spectra excited at 370 nm of PF8 co-colloids with HPS-S, -R, and type I HCPS-S ($x = 0.10$), and -R ($x = 0.10$) in the
cosolvents. PF8 with HPS-S reveals \((-\)-CPL signal originating from \(\beta\)-phase (not \(\alpha\)-phase) of PF8, conversely, with type I HCPS-S \((x = 0.10)\) reveals the opposite sign, \((+\)-CPL signal. Likewise, PF8 with HPS-R and HCPS-R \((x = 0.10)\) reveals \(\beta\)-phase-origin \((+\)-and \((-\)-CPL signals, respectively. Regardless of the same \((S)-(R)\)-chirality, the sign inversions in CPL and CD signals between PF8 co-colloids with HPS-S and type I HCPS-S \((x = 0.10)\) may arise from the same origin.

Figure 7. Cont.
Figure 7. (a) The CD and UV-visible spectra of PF8 co-colloids with HPS-S (blue lines) and -R (red line) in 1:1 mole ratio at 25 °C in MeOH-toluene cosolvent (1.5/1.5 (v/v)). (b) Their zoom-in CD and UV-visible spectra of PF8 region. (c) The CD and UV-visible spectra of PF8 co-colloids with type I HCPS-S (blue lines) and -R (red lines) (1:1 mole ratio) vs. mole fractions of the (S)-(R) in the cosolvent. (d,e) Their zoom-in CD and UV-visible spectra of type I HCPS-S and -R and PF8, respectively. (f) The \( g_{CD} \) values at 399–401 nm (α-phase) of PF8 (right ordinate, blue circles) and the \( g_{CD} \) values at 320–322 nm of type I HCPS-S and -R (left ordinate, red circles) vs. mole fractions of the (S)-(R) and (g) their zoom-in plots. (h) Comparisons of the CPL and PL spectra excited at 370 nm of PF8 co-colloids with HPS-S (dotted blue lines), -R (dotted red lines), type I HCPS-S (10%, solid blue lines), and -R (10%, solid red lines) (1:1 mole ratio) in the cosolvent. (i) The changes in CD and UV-visible spectra of PF8 co-colloids with type I HCPS-S (10%, blue lines) and -R (10%, red lines) (1:1 mole ratio) before (thin lines) and after (thick lines) the 313-nm photolysis for 600 s. (j) The zoom-in CD and UV-visible spectra of PF8. (k) Comparison of the CPL and PL spectra excited at 370 nm of PF8 co-colloids with HPS-S (blue lines) and -R (red lines) (1:1 mole ratio) before (thin lines) and after (thick lines) the 313-nm photolysis for 600 s. (l) Comparison of the CPL and PL spectra excited at 370 nm of PF8 co-colloids with type I HCPS-S (10%, blue lines) and -R (10%, red lines) (1:1 mole ratio) before (thin lines) and after (thick lines) the 313-nm photolysis for 600 s. The plots in Figure 7a,b,h (PF8 with HPS-S and -R), and Figure 7k are re-organized from the original datasets [67].

Upon application of 313-nm photolysis (14 µWcm\(^{-2}\), 600 s) in PF8 co-colloids with HPS-S and -R, the CPL signals of PF8 diminish by two-third relative to the original ones (Figure 7k) [67]. However, the CD and CPL signals of PF8 with type I HCPS-S (x = 0.10) and -R (x = 0.10) slightly diminish by 20–30% after the 313-nm photolysis, regardless of the (S)-(R) nature (Figure 7i,j,l). The anormal Ser-Sol effects of PF8 co-colloids with type I HCPS-S and -R are similar to the anormal Ser-Sol effects of PFV8 co-colloids with type I HCPS-S and -R, and type I HCPS-S and -R homo-colloids. The CPL and CPL signals of PF8 with the (S)-(R) considerably retain even after the 313-nm photolysis.

2.6. Majority Rule in PF8 Co-Colloids with Type II HCPS

The CD and UV-visible spectra of PF8 co-colloids with type II HCPS-SR with 1:2 in mole ratio in the MeOH-toluene (1.5/1.5 (v/v)) cosolvents with \( n_D \sim 1.415 \) are given in Figure 8a. HPS-S and -R in the co-colloids reveal the similar bisignate, couplet-like CD signals at the Si\( \sigma \)-Si\( \sigma^* \) transitions. From Figure 8b, PF8 in the co-colloids reveal the similar multiple couplet-like CD signals in the range of 350 nm and 450 nm originated from the α- and β-phases of PF8.
Figure 8. (a) The change in the CD and UV-visible spectra of co-colloids comprising PF8 and type II HCPS-SR \([S]/(R) = 0.60/0.40, 0.53/0.47, 0.50/0.50, 0.47/0.53, 0.40/0.60\) (2:1 in mole ratio) vs. mole fractions of the (S)-(R) in MeOH-CHCl₃ cosolvents (1/2, v/v). (b) Their zoom-in CD and UV-visible spectra. (c) The \(\xi_{CD}\) values (right ordinate, blue circles) at 399–401 nm (\(\alpha\)-phase) of PF8 and \(\xi_{CD}\) value (left ordinate, red circles) at 321–322 nm of type II HCPS-SR in the co-colloids vs. mole fractions of the (S)-(R). The data \([S]/(R) = 1.00/0.00\) and \(0.00/1.00\) in Figure 8a are taken from Figure 7b,c. (d) The CPL and PL spectra of PF8 co-colloids with type II HCPS-SR \([S]/(R) = 0.40/0.60\) (red lines), 0.50/0.50 (black lines), and 0.60/0.40 (blue lines]).

Figure 8c plots the \(\xi_{CD}\) values at 399–401 nm (\(\alpha\)-phase) of PF8 and at 321–322 nm (the first Cotton band) of type II HCPS in the co-colloids vs. mole fractions of the (S)-(R), respectively. The \(\xi_{CD}\) values between PF8 and type II HCPS in the co-colloids differ by 5–6 times. From the relation of the \(\xi_{CD}\) (PF8)–mole fractions of the (S)-(R), an anormal Maj-rule associated with sign-inversion between \([S]/(R) = 0.60/0.40\) and \(1.00/0.00\) and between \((S)/(R) = 0.00/0.60\) and \(0.00/1.00\) are occurring. The sign-inversion Maj-rule effect differs from that of PFV8 co-colloids with type II HCPS co-colloids and type II HCPS homo-colloids. The mole fractions of the (S)-(R) in type II HCPS are connected to generation of the CD-active PF8.

Figure 8d compares the three CPL and PL spectral sets of PF8 co-colloids with type II HCPS-SR (1:2 in mole ratio) with \([S]/(R) = 0.40/0.60, 0.50/0.50, 0.60/0.40\) in the co-solvent. The CPL spectral magnitudes of PF8–HCPS-SR with \((S)/(R) = 0.40/0.60\) are almost double relative to those of PF8–HCPS-SR with \((S)/(R) = 0.60/0.40\) while the CPL spectral magnitudes of PF8–HCPS-SR with \((S)/(R) = 0.50/0.50\) is not obvious. Thus, PF8 co-colloids with type II HCPS-SR show the anomalous Maj effects associated with sign inversion by the analysis of the CD and CPL spectra.

3. Discussion

3.1. Main-Chain Rigidity of HPS-S, HPS-R, HPS-IB, Type I HCPS, and Type II HCPS in Solution

Molecular physicists have been theoretically investigated for the possibility of parity-violation at molecular levels, called molecular parity-violation (MPV) [81–87]. The MPV hypothesis claims one-handed MSB because weak neutral current mediated by massive \(Z^0\) boson exists universally against a cosmic microwave background radiation of 2.73 K regardless of terrestrial and extraterrestrial origin. Most theories invoke that the degree of MPV is on the order of \(10^{-8}–10^{-14}\) kcal mol\(^{-1}\) for realistic and hypothetical molecules. Researchers interested in the MPV hypothesis often require experimentalists to show clear evidence by measuring such the ultra-tiny differences as the energy scales of enantiomeri-
cally pure vaporizable molecular pairs in a collision free, vacuum condition (of the order of \(\sim 0.1\) Pa), if possible, at cryogenic temperatures [86–89]. When the MPV hypothesis is valid, the enantiomers are no longer enantiomers and should be called diastereomers due to inherent energy inequality. Only enantiopure D-/L-oligomers with equal length, enantiopure D-/L-macromolecules with equal length, and right-hand (plus, \(P\))- and left-hand (minus, \(M\)) macromolecular helices with equal length are candidates to prove the MPV hypothesis although such high molecular mass substances cannot be vaporizable and decompose thermally at elevate temperatures.

Alternatively, macroscopic parity-violation (macro-PV) is considerably recognized as another parity-violation effects observable experimentally. The macro-PV indicates apparent mirror symmetry breaking at highly collision conditions; e.g.: (i) molecules, oligomers, supramolecules, and polymers dissolved in solutions, (ii) micelles, colloids, and aggregates as suspensions in liquids, (iii) gel states, and (iv) single crystals and polycrystals, time-dependent asymmetric synthetic reactions, and so on [90–99]. However, because macro-PV effects are often susceptible to enantiopurity of the \((S)-(R)\) [95] and/or a low level of putative impurities [94,97], molecular physicists rigorously distinguish between MPV and macro-PV effects; the macro-PV is not direct evidence of one-handed mirror symmetry at molecular level, meaning a handed chirogenesis [87].

Nevertheless, a pair of enantiomerically pure oligomers with the same sequences and equal lengths in pure solvents is feasible to experimentally validate the MPV hypothesis. In 2006, Shinitzky, Scolnik, and coworkers experimentally showed macro-PV effects in phase transition characteristics between D- and L-glutamic acid oligomers building up of 24 residues in water by means of precision isothermal titration calorimetry and CD spectroscopy [94]. The detectable differences in the physicochemical properties between the D-/L-oligopeptides were connected to the origin of L-amino acids, not D-amino acids, in water on Earth.

On the other hand, synthetic chiral/helical polymers are not ideal chiral macro-molecules with equal lengths to test MPV and macro-PV hypotheses. Most of all D-/L-chiral and/or \(P-/M\)-helical polymers are obtained as a mixture of various molecular weights. To overcome this drawback, one can compare several physicochemical characteristics between \(P-/M\)-helical main-chains and/or between \((R)-(S)\)-chirality as side-chains in solutions at specific temperatures using a narrow polydisperse specimens with similar molecular weights. Among several physicochemical methods achievable in ordinary laboratories, the viscometric data of chain-like polymers in dilute solutions as a function of molecular weights at specific temperatures and specific eluents by gel permeation chromatography (GPC), called GPC-VISCO, is one of the established reliable methodologies. GPC-VISCO data could support subtle differences in chiroptical properties of non-colloids in dilute solutions. The GPC-VISCO measurement allows for feasible approach to test the macro-PV and MPV hypotheses at individual macromolecular chain level. Because chromatographic grade pure solvents as achiral eluents can be used, the molecularly isolated chiral polymer chains under a forced flow condition are interacted only with achiral eluents like toluene and tetrahydrofuran.

The GPC-VISCO measurement provides dimensionality for a wide range of chain-like polymers in dilute solutions. The viscosity index \((\alpha)\) of the Kuhn-Mark-Houwink-Sakurada plots, \([\eta] = \kappa \cdot M^\alpha\), tells the degree of chain coiling for chain-like polymer at a given condition, where \([\eta]\) is an intrinsic viscosity at \(\text{conc} \to 0\), \(M\) is absolute molecular mass, \(\kappa\) is a constant [100–103]. The raw viscometric plots showing \(\alpha\) values as slopes of \(\text{HPS-H}_{-R}, \text{-IB, type I HCPS-S and -R, and type II HCPS-SR}\) in toluene at 70 °C are given in SI, Figures S9–S28. Additionally, TRC measured viscosity indices of two helical polymers possessing D- and L-chiral centers in the main chains, poly-\(\gamma\)-benzyl-L-glutamate (PBLG) and poly-\(\gamma\)-benzyl-D-glutamate (PBDG) (SI, Figures S29, S30) to verify reliability of differences in the intrinsic viscosity indices of our polysilanes. The viscosity indices of PBLG and PBDG in 0.05 M LiCl, DMF at 30 °C are 0.54 and 0.56, respectively, and nearly identical (SI, Figure S31).
Figure 9a plots the α value of HPS-S, -R, -1B, and type I HCPS-S and R as a function of mole fraction of the (S)-©. Likewise, Figure 9b is the α value of HPS-S and -R, and type II HCPS-SR as a function of mole fraction of the (S)-©. Evidently, all these polysilanes reveal high α values ranging from 0.96 and 1.81 and adopt rod-like or semi-flexible conformations in dilute toluene solutions. For example, a persistence length (q) of HPS-S with α = 1.24 in isooctane was evaluated to be 85 nm [97,98]. This higher q value corresponds to Kuhn’s segment length (l_K) of 170 nm.

Figure 9. The observed viscosity index (α) in toluene at 70 °C from the Kuhn-Mark-Houwink-Sakurada plots; [η] = η/ M^α, where [η] is the intrinsic viscosity, M the absolute molecular mass, and κ the constant. (a) Type I HCPS-S (blue circles) and -R (red circles) including HPS-S (blue circle, α = 1.24), -R (red circle, α = 1.52), and -1B (black square, α = 1.62) vs. mole fractions of the (S)-(R). (b) Type II HCPS-SR including HPS-S and -R vs. mole fractions of the (S)-(R). All data were adapted from SI, Figures S9–S28. The original α values and raw viscometric datasets of HPS-S and -R in toluene at 70 °C were disclosed in ref. [67]. The present paper first disclosed the raw viscometric datasets of type I HCPS and type II HCPS-SR. In 1990s, two research staffs without any foresight and scientific bias at Toray Research Center Co. (TRC, Shiga, Japan) obtained raw viscometric datasets in a series of P- and M-helical polysilane homo- and copolymers (SI, Figure S9–S28), carrying two (S)-(R) pendant pairs synthesized from 2-methylbutanol [(S) = 99.5 %ee and (R) = 100.0 %ee] [67,92] and 3,7-dimethyloctanol [(S) = 95.9 %ee and (R) = 95.7 %ee] [99], by the analysis of chiral gas-chromatography at TRC. These polysilanes were prepared by MF at NTT. Several researchers and MF at NTT in 1990s, who read their fact-base official reports, knew that the non-mirror-symmetrical CD and CPL spectra in solutions, as a colloidal suspension, and thin solid film are connected to the significant non-mirror-symmetric viscometric characteristics. The research team shared these facts due to unresolved reasons. MF reported the non-mirror-symmetrical viscometry, NMR spectra, and temperature-dependent UV/CD spectra of helix-helix and non-helix-helix transition polysilane homopolymers, that are connected to MPV hypothesis based on the Salam’s scenario [92,99].

From Figure 9a, one can be aware of the marked differences in the α-value vs. mole fractions of the (S)-(R) in type I HCPS. When a mole fraction of the (R) form increases from 0.007 to 0.25, the α value in type I HCPS tends to considerably decrease from 1.51 to 0.96, implicating marked shortening the q and l_K values. When a mole fraction of the (R) further increases to 0.50 and 1.00, the high α values of 0.76 and 1.81 suggest higher q and l_K values. Conversely, when mole fractions of the (S) increase from 0.006 to 1.00, the α value monotonously decreases from 1.60 to 1.24, suggesting gradual shortening q and l_K values.

Similarly, Figure 9b shows the marked differences in the α values vs. mole fractions of the (S)-(R) in type II HCPS. When a mole fraction of the (S) ranges from 1.00 and 0.50, the α value has an almost constant value of 1.24–1.35, therefore, the q and l_K values are nearly unchanged. On the other hand, when a mole fraction of the (R) form changes from 1.00 to 0.53, the α value increases from 1.52 to 1.76. The (R)-rich type II HCPS tends to adopt higher q and l_K values compared to the (S)-rich type II HCPS. The α value of type II HCPS [(S)/(R) = 0.50/0.50] is close to that of (S)-rich type II HCPS.

The changes in the α values connecting to the q and l_K values are not surprising. Compared to a short C–C single bond length of ~0.15 nm, a long Si–Si bond length of...
~0.23 nm results in a rotational barrier height as small as ~2 kcal mol\(^{-1}\) [103]. The small barrier height measures the internal steric demands between less bulky isobutyl and bulky 2-methylbutyl pendants. Therefore, to minimize to the steric repulsion, helical polysilane spontaneously alters the degree of chain coiling. Non-mirror-symmetrical viscosimetric characteristics between non-helix-helix transition HPS-S and -R, type I HCPS, and type II HCPS-SR could be also connected to the macro-PV effect mediated by handed inner-shell electrons interacting with the nucleus of helical polysilanes; the macro-PV effect may influence a subtle alteration in the main-chain stiffness and mobility [99].

Previously, MF reported non-mirror-symmetrical CD/UV-visible absorption characteristics of thermo-driven helix-helix phase transition behaviors for five pairs of helical polysilane homopolymers bearing (S)- and (R)-3,7-dimethyloctyl pendant pairs (96 %ee) in isooctane associated with their viscometric data [92,99]. The noticeable non-mirror-symmetrical CD/UV-visible characteristics in isooctane and chloroform ranging from −80 °C and +80 °C and detectable differences in chemical shifts and linewidths in \(^{29}\)Si/\(^{13}\)C-NMR spectra were ascribed to the macro-PV effects at polymer level; the chemical shifts of \(^{29}\)Si/\(^{13}\)C nuclei are perturbed by the degree of electron shielding near the nuclei and the linewidths are connected to Si–Si main-chain mobility.

3.2. Higher-Order Structures of Helical Polysilane Homo- and Copolymers in the Homo- and Co-Colloids

In the early 2000s, Okoshi, Watanabe, and coworkers elucidated that rod-like helical poly(n-decyl-(S)-2-methylbutylsilane) (DPS-S) afford cholesteric (Ch*) and smectic A phases; polydispersity index (PDI) = weight-average molecular weight (\(M_w\))/number-average molecular weight (\(M_n\)) and an aspect ratio of molecular length/molecular diameter are critical parameters in the condensed phases [63,104,105]. Because the PDI values of polysilanes used in this work range from 1.2 and 2.6 and the aspect ratio of molecular length/molecular diameter is greater than 50 (SI, Tables S1–S4), it is likely to form ill-ordered Ch*–like phase in the homo- and co-colloids. Actually, a clear couplet-like bisignate CD profile of DPS-S in thermotropic Ch*–phase at 80 °C [63] is very similar to the couplet-like bisignate CD profiles of HPS/HCPS homo-colloids and HPS/HCPS co-colloids with PFV8/PF8 as their suspension states at room temperature.

A preference in twisting direction in the colloids is primarily determined by side-chain chirality and main-chain helicity, that possibly work together collaboratively or non-collaboratively. In the type II HCPS-SR, main-chain helicity appears to be a dominant factor for chiroptical sense. In type I HCPS, main-chain helicity appears to be dominant for chiroptical sense when the mole fractions of the (S)-(R) range from 0.50 and 1.00 (Figure 2d). Conversely, side-chain chirality appears to be a deterministic factor for chiroptical sense when a mole fractions of the (S)-(R) ranges from 0.006(0.007) and 0.25 (Figure 2d). Other possible deterministic factor of chiroptical sense will be the aspect ratio of molecular length/molecular diameter that is exemplified for semi-flexible poly(alkylarylsilane)s [106] and rod-like poly(dialkylsilane)s [107]. A subtle change in diameter from bulkier 2-methylbutyl to less bulky isobutyl pendants causes the apparent chiroptical sense inversion (Figure 2c,d).

In recent years, Nagata and Suginome reported abnormal and normal Ser-Sol effects in a series of poly(quinoxaline-2,3-diyil)s (PQXs) with a very narrow PDI and almost same molecular weights when specific solvents are employed [55,56,108]. PQX copolymer carrying (S)-3-octyloxyethyl and n-propoxymethyl co-pendants reveals marked chiroptical inversion as functions of mole fractions of (S)-pendant chirality and molecular weight of PQXs when n-alkanes (alkyl length > longer than five) [108] were chosen. Solvent dependent bi-directional Ser-Sol effects in CHCl\(_3\), 1,1,2-trichloroethane, benzene, and toluene were also observed [55,56]. The uniqueness should arise from semi-flexibility of CD-silent racemic PQX helix carrying achiral pendant possessing \(q = 21\) nm and \(l_k = 43\) nm in tetrahydrofuran at 25 °C. Larger \(q\) and \(l_k\) values arise from lower barrier rotational heights of Ar–Ar, Ar–pendants, and intra-pendants [109]. However, a naive question remains to us; when helical pairs of PQX with the same (S)-(R) pairs were available, whether chiroptical
characteristics reveal rigorously mirror-symmetry. An apt question is whether viscometrical characteristics are precisely identical for P–M helical PQX pairs induced by the opposite (S)–(R) pendant chirality.

3.3. Possible Structures of Highly Emmisive PFV8 and PF8 in the Co-Colloids

Either HPS or HCPS are assumed to form helically ordered associations in co-colloids as the first step upon the addition of methanol as poor solvent. Helically ordered Ch*-like nanostructures may act as “seeds of chirality” and “seeds of helicity”, followed by propagation of helically twisted stacked structures from achiral PFV8 and PF8. It is known that PF8 and 9,9-alkyl derivatives adopt semi-flexible main chain that $q = 8.6 \text{ nm}$ and $l_k = 17 \text{ nm}$ in THF and $q = 7.0 \text{ nm}$ and $l_k = 14 \text{ nm}$ in toluene [78,110]. PF8 reveals a variety of higher order structures in the form of aggregates and in the solid films, depending on nature of alkyl pendants, choice of poor/good co-solvents, thermal treatment, and so on [78,80,111]. A highly emissive PF8 in dilute solution maintains highly emissive even in the aggregates and in the solid films [67]. Similarly, a highly emissive PFV8 in dilute solution maintains highly emissive property in the aggregates [70]. A plausible reason is owing to the intramolecular C–H/$\pi$ interaction existing commonly between fluorene $\pi$-ring and C–H$_2$ bonds at $\beta$- and $\gamma$-positions of $n$-octyl chains [112,113]. The built-in intramolecular C–H/$\pi$ interaction might prevent non-emissive $\pi$–$\pi$ stacks of PF-related polymers because of inherent bulkiness of two $n$-alkyl side chains at 9,9-positions of fluorene ring.

3.4. Co-Colloidal Stucture of PFV8 and HPS-S by Atomic Force Microscopy

From DLS analysis of PFV8 co-colloids with HPS-S in CHCl$_3$–MeOH cosolvents, a question remains whether PFV8 and HPS-S exist as individual segregates in the co-colloids. Imaging using atomic force microscopy (AFM) suggests that PFV8 and HPS-S onto HOPG are likely to exist as a mixture of PFV8 and HPS-S as their micro-colloids (SI, Figure S37). Larger domains are ascribed to HPS-S micro-colloids, and very small dots may be PFV8 micro-colloids.

3.5. Possible Inter-Macromolecular Interactions of PFV8/PF8 with HPS/HCPS in the Co-Colloids

Mulliken charges of 9,9-di-$n$-octylfluorenone vinylene dimer (FV8) and 9,9-di-$n$-octylfluorene dimer (F8), that are simple models of PFV8 and PF8, respectively, and $n$-hexyl-(S)-2-methylbutylsilane with permethyltetrasilane (PS-S), that is a simple model of HPS-S, obtained with DFT functional, B3LYP, 6-31G(d) basis set are displayed in Figure 10a–e. One can agree that PFV8 and PF8 are commonly non-polar structures without polar atoms. However, aromatic and aliphatic carbon atoms are commonly negative Mulliken charges (red color) while all hydrogen atoms attached to carbon atoms are positive Mulliken charges (green color). Likewise, HPS and HCPS are non-polar structures with no polar atoms in the side chains, excepting Si atoms in the main chain. Similarly, aliphatic carbon atoms are negative Mulliken charges (red color), conversely, all hydrogen atoms attached to carbon atoms are positive Mulliken charges (green color). Si atoms are intense positive Mulliken charges (green color).

The C–H/$\pi$ interaction, that are experimentally characterizable by crystallographic and NMR/infrared (IR) spectroscopic analyses and by theoretical simulations, is the most plausible inter-molecular interaction of PFV8/PF8 co-colloids with HPS/HCPS but appears not applicable to HPS/HCPS homo-colloids [114]. The most important term in the C–H/$\pi$ interactions between soft-base and soft-acid hydrogen bonding is the London dispersion force; nature favors delocalization by compensating opposite charges on atoms and groups tempo-spatially generated by a quantum fluctuation.
Figure 10. Mulliken charges of (a,b) FV8 dimer, (c,d) F8 dimer, and (e) PS-S, obtained with Gaussian09 (DFT functional with B3LYP, 6-31G(d) basis set).

Mulliken charge neutrality hypothesis proposed by us is applicable to various complex systems [23,24]; the hypothesis is similar to an exact charge neutrality of Coulombic interaction that is the key concept of a spontaneous association resulting from a long-range attractive force between polycations and polyanions [17]. The oppositely signed, but permanent Mulliken charges on atoms (marked as green and red color atoms) can feel intense attractive forces each other. Alkyl chain CH$_2$ atoms (green color) in the side chains of PS-S (Figure 10e) feel the attractive force from trans-vinylenes C=C double bond (red color) and six–seven aromatic carbons at fluorene rings of FV8 (Figure 10a,b). Likewise,
hydrogen atoms in CH$_2$ (green colors) in the side chains of PS-S feel the attractive force from six–seven aromatic carbons (red colors) at fluorene rings of F$_8$ (Figure 10c,d). These attractive forces led by the oppositely sign Mulliken charges on atoms between FV$_8$/F$_8$ and PS-S are assumed to be responsible for synchronized chirogenesis in the present co-colloidal systems.

However, what kind of inter-molecular interactions in HPS/HCPS homo-colloids can exist? Recently, the C–H/H–C interaction in the crystals was hypothesized by Hariharan [115]; dipolar/quadrupolar nature of sp$^2$ C–H bonding can induce a dipole on the vicinal sp$^3$ C–H bonding. The C–H/H–C interaction, though very weak, is possible to explain chirality/helicity transfer capability in the co-colloids from chiral aliphatic side-chains of HPS/HCPS to achiral aliphatic side-chains of PFV$_8$/PF$_8$. The attractive chiral–achiral interactions between chiral sp$^3$ C–H and achiral sp$^2$ C–H bondings appear more general in the liquid, colloidal, and condensed phases and widely applicable in the realm of supramolecular chirogenesis between non-polar aromatic and aliphatic molecules, oligomers, and polymers, that allowing to rationally designing sophisticated chiroptical functionality because aromatic (e.g., polyaromatic hydrocarbons (PAH)) and aliphatic hydrocarbons are ubiquitous on Earth and interstellar universe.

3.6. Film-State CD Spectra of PFV$_8$ with Type I HCPS and Type II HCPS

For practical applications, chiroptical functioned films based on Ser-Sol and Maj effects are inevitably needed. It is, however, difficult to characterize the detailed structure of the co-colloids due to the ill-defined structures. Disregard of Mulliken charge neutralization and C–H/H–C interaction hypotheses, these non-directional attractive weak interactions should help supra-macromolecular complexation between non-charged, non-polar π–conjugated polymers and non-charged, non-polar σ–conjugated polysilanes. Our approach is, however, beneficial to freely design solution processible supra-macromolecular complexation of two non-charged polymers with sophisticated chiroptical, electronic, and other functions in the future.

The changes in film-sate CD spectra of PFV$_8$ with type I HCPS deposited onto Tempax glass substate are given in SI, Figure S39a,b. The nearly mirror-symmetrical Ser-Sol effect can be seen, as SI, Figure S39a. On the other hand, from the changes in the film CD spectra of PFV$_8$ with type II HCPS, the non-mirror-symmetrical Maj effect appears as shown in SI, Figure S39b.

4. Perspectives

In an analogy to the chicken-or-the-egg question, the long-standing unanswered question in the realm of molecular biology might be the origin of life, which was the first, DNA or proteins? An answer was that ribozymes (ribonucleic acid enzymes) are capable of catalyzing functions in several biochemical reactions, like RNA splicing in gene expression [116]. Likewise, in connection to the origin of homochirality, which chirality was the first, DNA/RNA with D-chirality or proteins/polypeptides with L-chirality? [1–14]

More apt questions are the most fundamental questions of whether parity at biomolecular level is conserved or violated [8–14]; e.g., (i) whether D- and L-chirality are energetically equal, (ii) (S)- and (R)-chirality are energetically not different, and (iii) P- and M-helices are energetically equal.

Although P/M helicity is closely connected to D/L and/or (S)/(R) chirality of the building blocks, a preference in the helicity is changeable in response to external chemical and physical biases, e.g., known as salt-induced and thermo-driven B (right-hand helix)–Z (left-hand helix) transition of guanine-cytosine DNA [117]. Furthermore, from the viewpoint of chemical etiology based on base-paring capability as a probe of melting point ($T_m$), Eschenmoser questioned why Nature chose five-membered D-furanose, and not six-membered D-pyranose, in RNA and DNA [118]. His comprehensive result was that D-pyranose DNA (called homo-DNA) generates thermally stable Watson-Click type duplexes associated with an increase of $T_m$ by 30 °C, compared to D-furanose DNA. Similarly, D-
pyranose RNA forms the corresponding thermally stable homo-duplexes with an increase of $T_m$ by 30–60 °C. The outcomes led to the conclusion that a capability of thermally stable base-pairing of RNA and DNA is inefficient for non-enzymatic self-replication and template-directed copying under abiotic conditions.

By learning his conclusion, a proper flexibility and adaptability of chain-like polymers susceptible to alteration of external environments appears crucial in the colloidal processes. When one can view the main-chain rigidity between $(S)$- and $(R)$-derived helical polysilane homo- and copolymers, semi-flexibility of polysilanes bearing $(S)$-pendants with the lower $\alpha$ values are likely to form co-colloids with PFV8 and PF8 while more rigid polysilanes bearing $(R)$-pendants with the higher $\alpha$ values are not.

An obstacle of investigating an L-D preference of natural D-DNA and L-protein and their building blocks at laboratory level is to synthesize L-DNA and D-protein and/or to isolate enantiomerically pure forms using non-naturally occurring or naturally rare L- and D-bioresources associated with multiple-step synthesis maintaining enantiomerically high purity [91,93–97,119,120]. Among the rare studies of L- and D-proteins, absolute magnitudes such as molar ellipticity, $[\Theta]$, at two $\lambda_{ext}$ values (205 nm and 225 nm) between $\text{Fe}^{3+}$/$\text{L-rubredoxin}$ and $\text{Fe}^{3+}$/$\text{D-rubredoxin}$ and between apo-$\text{L-rubredoxin}$ and apo-$\text{D-rubredoxin}$ appear slightly different by approximately 20% and the absolute $[\Theta]$ values tend to bias to negative magnitudes [120]. The similar bias toward the negative CD amplitudes is reported for several macro-PV systems, including the microcrystalline solids [90] and helix-helix transition polysilanes in dilute solutions at cryogenic temperatures [99].

In our view, although the non-mirror-symmetric characteristics are not topics, the macro-PV effects may be seen already in several papers. For example, in 1993, Aoyama et al. reported that supramolecular complexes of non-rigid achiral resorcinol cyclic tetramer to bind several chiral aliphatic/aromatic alcohols in chloroform shows bisignate couplet-like CD bands at 270–310 nm at $\pi$–$\pi^*$ transition of the resorcinol; the CD amplitudes induced by the chiral guests are not ideal mirror symmetrical, and tend to shift toward negative-CD values by 8–240% disregard of $(S)$- and D-L chirality of three chiral alcohol pairs, in particular, non-rigid chiral alcohols boost the CD shifts [121]. Akagi et al. reported noticeable non-mirror-symmetric, couplet-like CD and CPL spectral profiles (magnitudes, $\lambda_{ext}$, and shapes) of three $\pi$–conjugated polymers in CHCl$_3$ solution; the $\xi_{\text{CPL}}$ values of the polymers are shifting to $(\pm)$-ones disregard of the $(S)$-$(R)$ pendant chirality and an absolute magnitudes between $(\pm)$- and $(\mp)$-CPL values differ by 1.3–2.1 times [122]. A similar tendency can be seen in other three polyacetylene derivatives carrying $(S)/(R)$ alkoxy pendant in CHCl$_3$; disregard of the $(S)/(R)$, the $\xi_{\text{CPL}}$ values tend to shift $(\pm)$-ones and an absolute magnitude between $(\pm)$- and $(\mp)$-CPL values differ by 1.5–1.7 times [123]. The $(\pm)$-shift in the $\xi_{\text{CPL}}$ values at 330 nm by 17% can be seen for a pair of $P$- and $M$-helical polysilanes, having $(S)$-2-methylbutyl/$n$-dodecyl and $(R)$-2-methylbutyl/$n$-dodecyl co-pendants, as their colloids in an optofluidic medium by ten set measurements of CPL/PL spectra [72].

In a recent paper reporting twistable peri-xanthenoanthene oligomers, non-mirror symmetric spectral shifts in CPL signals and different amplitudes/spectral shifts in couplet-like vibrational CD along with the corresponding unpolarized IR spectra can be seen [124,125]. Alternatively, in a recent paper of polyacetylene substituted with non-rigid binaphthyl pendants susceptible to molecular chirality of alkanes as guests in solutions, the CD signals at $\pi$–$\pi^*$ transitions at main-chain appear non-mirror-symmetrical associated with shifting toward $(\pm)$-CD values by 20–25% disregard of the guest $(S)/(R)$ chirality [126].

Researchers interested in the macro-PV hypothesis will encounter an inevitable drawback and difficulty because the $(S)/(R)$ substances with an extremely high enantiopurity of 100.00% or an extremely low enantio-impurity of less than 0.01% are in principle impossible to synthesize. They cannot provide definitive evidence to persuade scholars skeptical about the macro-MPV and MPV hypotheses.

To overcome these difficulties, an alternative approach is to utilize non-rigid, dynamically twisting racemic substances available commercially and/or prepared/purified in...
a short-step synthesis. Classically, in non-rigid, diprotonated tetrathenylsulfonate porphyrins upon application of clockwise and counter-clockwise vortex flowing, one may recognize non-mirror symmetric amplitudes associated with unequal amplitudes and spectral shapes at two couplet-like CD signals at B-band at ~480 nm and Q-bands at ~720 nm, respectively though the macro-PV was not the topic [127]. Recently, on the basis of the MPV hypothesis, by measuring a heat capacity with adiabatic calorimeter and spin-lattice $T_1$ time with $^1$H-NMR down to cryogenic temperatures (9–300 K), Kozlova and Gabuda showed an occurrence of quantum-tunneling assisted MSB below 60 K of Zn$^{II}$-containing organic framework consisting of $D_3$-symmetric 1,4-diazabicyclo[2.2.2]octane (well-known as DABCO) twistable between left-and-right in a double-well potential [128]. Although an apt question remains which ($S$)- or ($R$)-crystal is stabilized below 60 K, a further clarification is awaited. Presumably, the crystal shows intense ($-$)-CD signal below 60 K, weak ($-$)-CD or weak (+)-CD signal above 60 K, and zero-CD signal at room temperature.

Our recent papers reported handed CPL signals showing only negative-sign in the photoexcited states, that means handed photochirogenesis, from approximately sixty non-rigid rotamers including molecules, oligomers, and polymer, that do not have stereogenic centers, in achiral dilute solutions [129–131]; spontaneous radiation/relaxation processes associated with structural reorganization at the photoexcited states, rather than absorption processes, are susceptible to unveil the macro-PV as non-racemic metastable structure as a handed chirogenesis. Note that the CPL and CD spectrometers used in these works were certified by non-detectable CD/CPL signals of several achiral rigid $\pi$-conjugated aromatic molecules along with ideal mirror-symmetry CD- and CPL-spectra (amplitudes, sign, wavelengths, and shapes) of very rigid molecular($1S$)-($-$)/($1R$)-($+$)-camphor.

Based on our comprehensive results of helical/chiral polysilanes in the present paper, pendant chirality and/or main-chain helicity of photoscissable HPS/HCPs efficiently worked as chirality/helicity scaffolding to non-photoscissable achiral/non-helical PFV8/PF8. Inter-chirality/main-chain helicity capability between two polymers, that are mimicking optically inactive oligopeptide with optically active sugars, conversely, optically inactive sugars with optically active oligopeptide, are likely to occur in a synchronized manner in coacervates-like co-colloidal systems in aqueous condition. Regarding main-chain rigidity, chain-like polymers adopting semi-flexibility might enable an adaptability to any alterations, like self-replication, self-repairing, and catalytic capabilities. The (S)-chirality, originating from naturally occurring starting source, tends to provide the lower viscosity indices in a series of type II HCPs-RS, compared to (R)-one prepared from non-naturally occurring source. Possibly, a very rigid, non-twistable helix made of non-naturally occurring constituents may lack such the adaptability. To provide a proper semi-flexibility, biomacromolecules consisting of the naturally-occurring D-chirality in sugars and L-chirality in amino acids are assumed to be pre-determined, for example, endowed with parity-violating weak neutral current force in the ground and photoexcited states of atoms and sub-atoms existing in whole universe [99,129–131]. The colloidal particle dispersed in an optofluidic medium efficiently works as chiroptical resonator endowed with WGM [25], enabling to boost ultra-small non-detectable MPV effect on the order of $10^{-8}$–$10^{-14}$ kcal mol$^{-1}$ to a detectable level as macro-MPV effects.

5. Methods and Materials

5.1. Instrumentation

The CD and UV-visible spectra were recorded simultaneously at 20 °C by a J-820 spectropolarimeter (JASCO, Hachioji, Tokyo, Japan) using rectangular quartz cuvettes (path lengths: 5 mm and 10 mm) at ambient temperature. To obtain precise CD/UV-visible spectra, a scanning rate of 50 and 100 nm min$^{-1}$, a bandwidth of 2 nm, a response time of 2 s and 1 or 2 accumulations were employed. The instrument was aged for at least 2 h to minimize drifts of the power supply and light source. Likewise, the CPL/CPL/PL spectra were collected on a JASCO CPL-200 spectrofluoropolarimeter using the rectangular cuvettes (path lengths of 5 mm and 10 mm) at room temperature (approximately 20–25 °C). The optimal
experimental parameters were that scanning rate = 20–50 nm min⁻¹; bandwidth = 10 nm for excitation and detection; response time of PMT = 8–16 s during measurements and 2 to 8 accumulations. Technically, all the CD and UV-visible spectra including rectangular quartz cuvette and co-solvents in the presence of as-prepared colloids were automatically obtained solely by subtracting the corresponding CD and UV-visible spectra of the same co-solvents with the same cuvette in the absence of the colloids, that are saved as temporal memory each time on J-820 computer program, followed by no further processing on the computer and converted as their text data enable to plots using the KaleidaGraph software (Mac ver. 4.53, Synergy (Reading, PA, USA)). Note that the baseline noises in Figure 2, Figure 3, Figure 4, Figure 5, Figure 6, Figure 7, Figure 8 and are thus as-is without further processing like numerical smoothing.

The dissymmetry ratio, $g_{CD}$, was evaluated by the equation that $g_{CD} = \Delta \varepsilon / \varepsilon = \text{ellipticity (in mdeg)/[absorbance]} / 32,980$ at $\lambda_{ext}$ or $g_{CD} = (\varepsilon_L - \varepsilon_R) / (\varepsilon_L + \varepsilon_R)/2$, where $\varepsilon_L$ and $\varepsilon_R$ are the extinction coefficients for left- and right-CP light, respectively. To calculate $g_{CD}$, CD and UV/UV-visible signals at the same $\lambda_{ext}$ of the CD signals are used. Likewise, the dissymmetry ratio of circular polarization at the $S_1$ state ($g_{CPL}$) was calculated by the equation that $g_{CPL} = \Delta I/I = (I_L - I_R)/[I_L + I_R]/2 = \text{[ellipticity (in mdeg)/(32,980/Lin10)]/[total PL intensity [in Volts]]}$ at CPL extremum ($\lambda_{ext}$), where $I_L$ and $I_R$ are the signals for left- and right-CP light under the unpolarized incident light, respectively. To evaluate the $g_{CPL}$ value, CPL and PL signals at the same $\lambda_{ext}$ of the CPL signal were used.

The polysilanes and their dichlorosilane source materials were characterized by the $^{29}$Si- (59.59 MHz) and $^{13}$C- (75.43 MHz) NMR spectroscopy in CDCl₃ at 30 °C using a Unity 300 MHz NMR spectrometer (set-up at NTT in the 1990s, Varian, as a member of Agilent Technologies, Palo Alto, CA, USA) with tetramethylsilane as an internal standard.

The weight-average molecular weight ($M_w$), number-average molecular weight of the polymers ($M_n$), and polydispersity index ($PDI = M_w/M_n$) were evaluated using gel-permeation chromatography (A10 chromatograph, Shimadzu, Kyoto, Japan) using a Shodex KF-806M column (Showa Denko, Tokyo, Japan) and a PLGel mixed B column (25 cm in length, 4.6 mm ID (Agilent Technology Japan, Hachioji, Tokyo, Japan). HPLC-grade THF (Wako Chemical, Osaka, Japan) was used as the eluent, and the data were calibrated on the basis of the polystyrene standards (Varian-Agilent). All polysilanes and the corresponding dichlorosilane monomers used in this work were synthesized and characterized from 1992 March and 1992 June when one of the authors (MF) worked for NTT basic research laboratory. All polysilanes were stored in sealed vials in the dark at room temperature over 20 years. Prior to initiate the present study, these polysilanes did not decompose associated without auto-oxidation. In doubly sure, these $M_n$, $M_w$, and $PDI$ at NAIST were re-measured prior to investigate the present works.

The $[\eta] - M$ relationship of polysilane homo- and copolymers used in this work in dilute toluene at 70 °C was measured at Toray Research Center (TRC, Shiga, Japan) and NTT R&D Center using a 1500 GPC apparatus (Waters, Milford, MA, USA) with three GMHXL columns (30 cm × 8 mm ID, Tosoh, Tokyo, Japan) at a flow rate of 0.97 mL min⁻¹ equipped with a Viscomet, now, Malvern Panalytical, Malvern, UK) H502a viscometer. All the results as in-house datasets in those days were obtained and confirmed by colleagues when MF worked for NTT basic research laboratory.

Dynamic force mode (DFM) atomic force microscopy (AFM) images were captured using a SPA 400 SPM unit with a SII SPI 3800 probe station (Seiko Instruments, Inc., now Hitachi High-Tech Science Corp., Tokyo, Japan). The sample was deposited onto a HOPG substrate (IBS-MikroMasch, Sofia, Bulgaria; a Japanese vendor is Tomoe Engineering Co., Tokyo, Japan) by dropping the colloids suspension into a mixed methanol-chloroform solvent. The deposited specimens were measured after the solvent was removed.

The colloids sizes were analysed by dynamic light scattering (DLS) (a detector with 90°, 30 accumulated scans; Otsuka Electronics (Hirakata-Osaka, Japan) model DLS-6000 using solution viscosity data obtained with a Sekonic (Tokyo, Japan) viscometer VM-100 at 25 °C, along with the $n_D$ value of methanol-toluene (1.5:1.5 (v/v)) and methanol-chloroform
was added. To the CHCl$_3$ solution (2.0 mL), a 1.0 mL of MeOH was slowly added and methanol afforded narrower PDI overnight at 120 $^\circ$C. All molecular weight characteristics were listed in SI, Tables S1–S3 (p. 6 and p. 8).

The main chain lengths of $\text{HPS-S}$, $\text{HPS-R}$, $\text{Type I HCPS-S}$, $\text{Type II HCPS-S}$, $\text{PFV8}$, and $\text{PF8}$ were evaluated by the product of their monomer unit lengths and number-average degree of polymerization $D_P = M_n/M_0$, where $M_n$ and $M_0$ are the number-average of molecular weight and the molecular weight of the monomer unit.

5.2. Preparation and Fractionation of Polysilanes and the Corresponding Dialkyldichlorosilanes

Synthesis and characterization of poly(n-hexyl-(S)-2-methylbutylsilane) ($\text{HPS-S}$), poly(n-hexyl-(R)-2-methylbutylsilane) ($\text{HPS-R}$), poly(n-hexyl-isobutylsilane) ($\text{HPS-IB}$), poly(n-hexyl-rac-2-methylbutylsilane) ($\text{HCPS-SR}$) and their dialkyldichlorosilanes as monomers ($^{29}\text{Si}-^{13}\text{C}$-NMR) were described in SI (pp. 7–18). Synthesis and characterization of all dialkylpolysilanes (molecular weights, molecular length, and viscosity indices in toluene at 70 $^\circ$C) were described in SI (pp. 1–7).

5.3. Fractionations of $\text{PFV8}$, $\text{PF8}$, and Polysilanes

The fractionation processes and molecular weight characteristics of $\text{PFV8}$ [69] and $\text{PF8}$ [67] were briefly given in supplementary materials, Section Fractionation of $\text{PFV8}$ and $\text{PF8}$ used in this work (S2-7), Table S4. In case of polysilanes, a broad molecular weight dispersity of samples was fractionated by slowly adding isopropanol (IPA) during gentle stirring until the colloid was generated. White precipitates were collected by a centrifugation with a 5420 centrifuge (Kubota, Tokyo, Japan) at 3000 rpm, followed by drying overnight at 120 $^\circ$C under vacuum. As for the clear solution, a further fractionation with ethanol and methanol afforded narrower $PDI$ samples was carried out. White precipitates were collected by centrifugation with the centrifuge at 3000 rpm, followed by drying overnight at 120 $^\circ$C under vacuum. All molecular weight characteristics were listed in SI, Tables S1–S3 (p. 6 and p. 8).

5.4. Preparing $\text{PFV8}$ and $\text{PF8}$ Co-Colloids with $\text{HPS}$, $\text{Type I HCPS}$, and $\text{Type II HCPS}$

Spectroscopic-grade toluene and chloroform (Dojindo, Kumamoto, Japan) as good solvents and methanol (Dojindo) as a poor solvent were added to produce an optically active co-colloids in a 10 mm synthetic quartz (SQ)-grade quartz cuvette. The optimized volume ratio of $\text{PFV8}$ experiments was 2.0:1.0 with the total volume content of mixed chloroform and methanol being fixed at 3.0 mL. The optimized volume ratio of $\text{PF8}$ experiments was 1.5:1.5 with the total volume content of mixed toluene and methanol being fixed at 3.0 mL. The molar ratio of the polymers in dissolved chloroform ($\text{PFV8}$) or toluene ($\text{PF8}$) was tuned according to the experimental requirements. The detailed protocols are as follows.

$\text{PFV8}$ co-colloids: To a mixed solution (total; 0.3 mL) of $\text{PFV8}$ (stock solution; [conc]$ = 2.0 \times 10^{-4}$ M$^{-1}$ in CHCl$_3$ as repeating unit) and $\text{HPS/Type I HCPS}$ (stock solution; [conc]$ = 2.0 \times 10^{-4}$ M$^{-1}$ in CHCl$_3$ as repeating unit) in the cuvette, a 1.7 mL of CHCl$_3$ was added. To the CHCl$_3$ solution (2.0 mL), a 1.0 mL of MeOH was slowly added to generate yellow colloidal particles. The solution including colloids was processed by
shaking up-and-down five times, enabling to a well-mixed good-and-poor cosolvent and co-colloids dispersed homogeneously in the co-solvent.

**PF8** co-colloids: To a mixed solution (total; 1.5 mL) of **PF8** (stock solution; [conc]₀ = 2.0 × 10⁻⁴ M⁻¹ in toluene as repeating unit, 0.75 mL) and **HPS/Type II HCPS** (stock solution; [conc]₀ = 2.0 × 10⁻⁴ M⁻¹ in toluene, 0.75 mL) in the cuvette, a 1.5 mL of MeOH was slowly added by the shaking process to generate pale-yellow co-colloids dispersed in the co-solvent.

**HPS/HCPS** homo-colloids: To a 0.3 mL solution of **HPS/Type II HCPS** (stock solution; [conc]₀ = 2.0 × 10⁻⁴ M⁻¹ in CHCl₃ as repeating unit) in the cuvette, a 1.7 mL of CHCl₃ was added. To the solution, a 1.0 mL of MeOH was slowly added to generate white colloidal particles. The mixtures was further treated by the shaking process, producing a well dispersed homo-colloids in the co-solvent.

Simultaneously, CD/UV-visible and CPL/PL spectroscopic data were collected within several minutes after completion of the co-colloidal process.

5.5. Optimizing Optofluidic Effect of **PFV8** Co-Colloids with **HPS-S**

In designing the controlled optofluidic co-colloidal systems including helical polysilane copolymers, **PFV8**, and a mixture of the surrounding poor-good co-solvents, the best mole ratios of helical poly(n-hexyl-(S)-2-methylbutylsilane), **HPS-S**, and **PFV8** and the best volume fraction in a mixture of the cosolvent enable to effectively confine light energy inside of the co-colloid were optimized (SI, Figure S40).

5.6. Choosing Good-and-Poor Co-Solvent to Maximize Ser-Sol and Maj Effects of **PFV8** and **PF8** Co-Colloids with **HPS and Type I HCPS**

To maximize Ser-Sol effect of **PFV8** co-colloids with **HPS and Type I HCPS**, the effects of three poor-good co-solvents (fixed to 2/1 (v/v)) that enable to effectively boost CD signals of \( \pi-\pi^* \) transitions of **PFV8** are given in Figure 4 in the main text and SI, Figure S41–S42. The values of \( |g_{CD}| \) at ~460 nm of **PFV8** are in the order of CHCl₃–MeOH co-solvent ((50–100) × 10⁻³) >> toluene–MeOH co-solvent (~2 × 10⁻³) > THF–MeOH co-solvent [0.6 – 0.9] × 10⁻³. Chiroptical inversion between 25 mol % and 50 mol % of the (S)- (R) pendant chirality was commonly occurred regardless of the three cosolvents. The CHCl₃–MeOH co-solvent was therefore used for Maj effect experiments of **PFV8** co-colloids with **Type II HCPS**. In Ser-Sol and Maj effect experiments of **PF8** with **Type I HCPS**, toluene–MeOH co-solvent was chosen after an initial screening of the \( |g_{CD}| \) values of **PF8** co-colloids with **HPS-S** in two CHCl₃–MeOH and toluene–MeOH co-solvents because CHCl₃–MeOH cosolvents with several ratios generated the CD-/CPL active **PF8** co-colloids with **HPS-S** though the \( |g_{CD}| \) values of **PF8** weakened slightly [67].

5.7. Calculating Mulliken Charges for Oligomeric Models of **HPS-S, PFV8, and PF8**

Computer generated pentamer model of **HPS-S** with P-7₃ helix (dihedral angle \( \approx 155^\circ \)), **PFV8**, and **PF8** (dihedral angle \( \approx 150^\circ \)) were optimized with PM3-MM (Gaussian09 rev. D.01, Gaussian, Inc., Wallingford, CT, USA, 2013) running on an Apple PowerMac (2.93 GHz clock, 16-cores, and 64 GB memory).

6. Conclusions

It is known that non-charged semi-flexible and rod-like helical copolymers and \( \pi-\pi \) molecular stacks reveal sergeants-and-soldiers (Ser-Sol) and majority-rule (Maj) effects in dilute solutions and as a suspension in fluidic liquids. A question remained unanswered whether Ser-Sol and Maj effects between non-charged rod-like helical polysilane copolymers and non-charged, non-helical \( \pi \)-conjugated homopolymers occur when these polysilane copolymers encounter the \( \pi \)-polymer in the co-colloidal systems. To address the questions, the present study used two types of polysilane copolymers, carrying (i) (S)- or (R)-2-methylbutyl with isobutyl groups as chiral/achiral co-pendants (**Type I HCPS**) and (ii) (S)- and (R)-2-methylbutyl groups as chiral/chiral co-pendants (**Type II HCPS**). For the \( \pi \)-polymers, poly[(diocylfluorene)-alt-(trans-vinylene)] (PFV8) and poly(diocylfluorene)
(PF8) as blue luminescent polymers were chosen. Detailed analyses of circular dichroism (CD), circularly polarized luminescence (CPL), and CPL excitation (CPLE) spectroscopic datasets revealed noticeable chiroptical inversion in the Ser-Sol effects of PFV8/PF8 co-colloids with type I HCPS. The normal Maj effect of PFV8 co-colloids with type II HCPS was observed though PF8 co-colloids with type II HCPS showed an anormal Maj effect revealing a chiroptical inversion. The behaviors in the Ser-Sol and Maj effects were synchronized with the natures of type I HCPS and type II HCPS homo-colloids. The CD/CPL-active PFV8/PF8 co-colloids with types I/II HCPSs resulted in the corresponding CD/CPL-active PFV8/PF8 homo-colloids by photochemically removal of photoscissable types I/II HCPSs upon irradiation at 313 nm. Certain intermolecular C–H/π and C–H/H–C interactions were assumed to be responsible for the synchronized chirogenesis between PFV8/PF8 and types I/II HCPSs. The present paper discussed the origins of noticeable non-mirror-symmetrical Ser-Sol and Maj effects in terms of macroscopic parity-violation that differs from a rigorous criteria of molecular parity-violation hypothesis. Our comprehensive helicity/chirality transfer experiments associated with significantly enhancements in the CD-and-CPL signals at the ground and photoexcited states of artificial helical/non-helical polymer co-colloids in the tuned refractive index optofluidic media led to propose possible answers to several unresolved questions in the realms of molecular biology, stereochemistry, supramolecular chemistry, and polymer chemistry; (i) whether mirror symmetry on macroscopic levels is rigorously conserved, (ii) why Nature chose L-amino acids and five-membered D-furanose (not six-membered D-pyranose) in DNA/RNA.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/sym13040594/s1. Preparation and characterization of polymers and monomers, DLS results, viscometric datasets of all polysilanes used in this work and PBLG/PBDG for comparison, AFM image onto HOPG, and CD/UV-visible spectra of PFV8 with type I HCPS and with type II HCPS in the film state deposit on Schott AG (Mainz, Germany) Tempax Float® solid glass substrate.

Author Contributions: M.F., S.O. and N.A.A.R. have employed to examine the sergeants-and-soldiers and majority-rule of achiral/non-helical PFV8 and PF8 endowed with helical type I HCPS and type II HCPS when they were assorted as co-colloids in optically tuned optofluidic media. M.F. designed the application of CPL/CD spectroscopy to test sergeants-and-soldiers and majority-rule effects. T.Y. and K.N. provided a fresh PFV8 synthesized with a narrower polydispersity to test our experiments and intimately discussed based on our recent publication of CD and CPL characteristics of several PFVs carrying different chiral pendants as colloidal systems. M.F., S.O., and N.A.A.R. measured and analyzed CD, CPL, and CPLE spectroscopic datasets. M.F., N.A.A.R., and K.N. cowrote the manuscript. All authors have read and agreed to the published version of the manuscript.

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