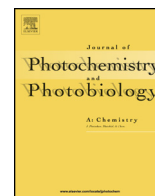




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Tempo-spatial chirogenesis. Limonene-induced mirror symmetry breaking of Si—Si bond polymers during aggregation in chiral fluidic media

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Dedicated to Prof. Yoshihisa Inoue, who discovered entropy driven chirogenesis and is a seeker for the origin of homochirality on the Earth.

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Symmetry breaking
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ABSTRACT

Herein, we designed photoluminescent polymer aggregates surrounded by organic media containing (*S*)-/(*R*)-limonene and (1*S*)-/(1*R*)- α -pinene as an artificial model of an open-flow cell-wall free coacervate in a fluidic medium in the ground and photoexcited states. The aggregates were build-up of stiff circular dichroism (CD)-silent and circularly polarized luminescence (CPL)-silent bis(*p*-*n*-butylphenyl)polysilanes, **nBuPS**, and four other diarylpolsilanes. (*S*)- and (*R*)-limonene induced more efficiently to their chirality to **nBuPS** during aggregation, as proven by CD and CPL spectral analysis, compared to (1*S*)- and (1*R*)- α -pinene. The **nBuPS** aggregates generated in a mixture of limonene, methanol, and chloroform had a dissymmetry factor (g_{abs}) as high as +0.04 for (*R*)-limonene and -0.03 for (*S*)-limonene at the first Cotton band and a weak dissymmetry factor (g_{lum}) of +0.004 for (*R*)-limonene and -0.003 for (*S*)-limonene. The g_{abs} factor, however, greatly depended on the volume fraction and chirality of limonene in the tersolvents. These behaviors were ascribed to the tempo-spatial stability and instability of the aggregates suspension in the fluidic media, as revealed by time-course dynamic light scattering measurement.

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1. Introduction

In astronomy, astrochemistry, astrobiology, and astrophysics, researchers seeking extra-terrestrial life have long assumed that liquid water is inevitably needed for the evolution of life. In 2013, Hubble space telescope (NASA) captured geysers of liquid water from Europa covered with a crust of thick ice, one of the Jupiter family [1]. The most spectacular events in 2014 might be discoveries of several exoplanets located in habitable zones [2–6]. Kepler (NASA) indicated that several habitable exoplanets, named super-earths, exist [2]. Super-earth means that the planet's size is almost comparable to that of our Earth. Kepler found the first super-earth with 1.2-Earth-radius, named Kepler-186f [3]. Tau Ceti e, the nearest super-earth 11.9 light-years away from us, is estimated to have an average surface temperature of $\approx 70^\circ\text{C}$ [4]. Moreover, Cassini (a part of Cassini–Huygens missions of NASA)

using a quadrupole gravity measurement system discovered water under the surface of Enkelados, one of 67 Saturnian moons [5]. The Jet Propulsion Laboratory at NASA concludes that Titan, the largest Saturnian moon, has extremely salty water involving inorganic salts of sulfur, sodium, and potassium [6]. Rosetta (ESA) invoked the detection of prebiotic constituents involving water, several organic fragments, and SiO_2 by a direct landing on comet 67P/Churyumov-Gerasimenko, the Jupiter family [7,8]. In 2015, NASA confirmed that liquid water, though containing $\text{Ca}(\text{ClO}_4)_2$, $\text{Mg}(\text{ClO}_4)_2$, and NaClO_4 salts, is still flowing on the surface of Mars by the detection of water-related $1.4\ \mu\text{m}$ and $1.9\ \mu\text{m}$ bands in the near-infrared region [9].

If life existed in the past or is now existing on these exoplanets, solar planets, moons, and comets, a big question with a great curiosity is whether *S*-/*R*-point chirality (stereogenic centers) and/or *P*-/*M*-helicity (stereogenic bonds) are identical to those on our Earth [10,11]. Living organisms are always tempo-spatial and metastable as a consequence of far-from-equilibrium open system [12]. Life can survive only under open flows of energy and chemical sources because life eats low-entropy food and solar energy [13].

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The origin of homochirality on the Earth has been a mystery in the modern scientific community over 150 years [10,14–24] because life cannot exist without molecular asymmetry [14]. So far, many scientists have proposed several plausible scenarios from the primordial era to answer this big question. Scientists have long argued about the possibility of exo-terrestrial life [10,15–22] as well as the origin of life on Earth. Circularly polarized radiation sources, such as γ -ray, X-ray, and vacuum UV, may become a trigger for the left-right selection of biomolecular substances [15–22]. In 1969, mankind received an incredible gift of carbonaceous stone, known as the Murchison meteorite, from the interstellar Universe [25]. The meteorite was contaminated with terrestrial origin amino acids, of which *L*-enantiomers were in excess over *D*-ones, revealed by a largely enriched ^{15}N in $^{15}\text{N}/^{14}\text{N}$ ratio and marked depletions of ^{13}C in $^{13}\text{C}/^{12}\text{C}$ ratio and D in D/H ratio, relative to the biological origin amino acids on the Earth [26,27]. A recent study demonstrated that a subtle imbalance in *L*-/*D*-amino acids can catalyze the asymmetric generation of carbohydrates with a high *ee*, which might be responsible for the homochiral world [28]. Moreover, even nearly racemic substances with $10^{-5}\%$ *ee* can be significantly amplified to nearly 100% *ee*, as exemplified by the Soai-reaction [29].

The homochirality question, however, is a difficult one because of a complete lack of any fossil record or trace amount of chiral molecular evidence. However, marked depletion of ^{13}C in $^{13}\text{C}/^{12}\text{C}$ -isotopic ratio suggests evidence that methanogenic microbial existed in the Archaean era at least 3.5–3.8 Gyrs ago [30–32]. This conclusion was drawn from the fact that lighter ^{12}C -containing substances in living organisms are enriched during their entire lifetime. Moreover, the recent snowball Earth hypothesis with analysis of palaeomagnetism asserts that Prokaryotes only inhabited Precambrian eras for more than 2 Gyrs [33,34], though critical argument has been still made to the radical hypothesis [35].

In 1920s–1930s, a more radical idea was hypothesized by Oparin in Russia [36] and Haldane in UK [37]. They independently claimed that the coacervate is a prototype of living cells during the chemical evolution of life. The coacervate refers to spherical aggregates surrounded by water – colloidal droplets – made of stable organic matter, followed by spontaneous growing and fermentation. This hypothesis relies on spontaneous association during liquid–liquid phase separation resulting from non-covalent electrostatic, hydrogen bonding, and van der Waals interactions. Coacervate size typically ranges from 1 to 100 μm in diameter, almost identical to that of living cells. However, the hypothesis was mostly abandoned because coacervate did not evolve living life. At the time, although colloids made of low-molecular mass organic matter were commonly known among scientists, high-molecular

mass molecules exceeding 10,000 proposed by Staudinger were not widely accepted [38]. Nowadays, high molecular mass molecules are commonly known as polymers and macromolecules.

Most hypotheses assumed coacervate to be rigid hard particles surrounded by water without any flows of energy and chemical substances. If coacervates can adopt a more dynamic structure like a swollen gel, this soft matter system should be adaptable to any alterations of external biases, allowing flows of chiral chemical and circularly polarized photon energy sources. This idea led us to design a cell-wall free, semi-artificial coacervate model built up from chain-like synthetic polymers surrounded by a mixture of chiral and achiral organic solvents. This open system allows investigation of tempo-spatial molecular chirality transcription of the soft aggregates. Particularly, time-dependent alteration in the size of optically active aggregates becomes measurable because optically active aggregation becomes popular in recent years [39–54].

Aiming at realizing the soft matter coacervate system enabling open flows of chiral substances in the ground state and/or circularly polarized radiation in the photoexcited state, the following five bis(*p*-alkylphenyl)polysilanes, were chosen: **nBuPS**, **EtPS**, **iPrPS**, **tBuPS**, and **tBuPS** (Fig. 1). These Si–Si bond polymers are non-charged chromophores and luminophores made of multiple stereogenic bonds. Although the first synthesis of **nBuPS** was reported by Miller and Sooriyakumaran three decades ago, **nBuPS** is shown to adopt a notably stiff backbone with a persistence length (*q*) of ≈ 10 nm, which is one third relative to the *q* of double-strand DNA [55,56]. The long *q* value means that ≈ 55 repeating **nBuPS** units behave as an ideal rod. The other four **EtPS**, **iPrPS**, **tBuPS**, and **tBuPS** possibly adopt a similar stiff backbone because they commonly have bulky diaryl groups attached to the backbone. Non-polar (*S*)-/(*R*)-limonene and (*1S*)-/(*1R*)- α -pinene were chosen as chiral terpenes because limonene and α -pinene are efficient stereogenic center transferable solvents for several circular dichroism (CD)-silent and/or circularly polarized light (CPL)-silent π - and σ -conjugated polymers [44,49–54]. CD-active and/or CPL-active aggregation of these polymers occurs with the help of van der Waals force only with these terpenes. Aggregation behavior is characterized because $\text{Si}\sigma\text{--Si}\sigma^*$ transitions, characteristic of diarylpolysilanes, are chiroptical probes to detect chiralities in the ground- and photoexcited states of the backbones [56–58]. Compared to $\pi\text{--}\pi^*$ transitions associated with phonon side bands, very narrow structure-less $\text{Si}\sigma\text{--Si}\sigma^*$ transition spectral bands facilitate to detect subtle imbalance between *P*- and *M*-motifs and helical pitch, that are detectable by CD and CPL spectroscopies, and dynamic light scattering (DLS) and fluorescence optical microscopy (FOM) methods.

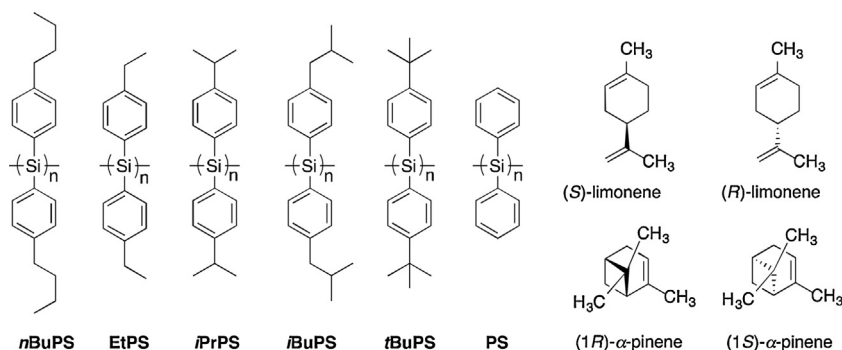


Fig. 1. Chemical structures of diarylpolysilanes, limonene, and α -pinene used in this work.

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