

Review

Supramolecular Chirality: Solvent Chirality Transfer in Molecular Chemistry and Polymer Chemistry

Michiya Fujiki

Graduate School of Materials Science, Nara Institute of Science and Technology (NAIST),
8916-5 Takayama, Ikoma, Nara 630-0036, Japan; E-Mail: fujikim@ms.naist.jp;
Tel.: +81-743-72-6040

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Abstract: Controlled mirror symmetry breaking arising from chemical and physical origin is currently one of the hottest issues in the field of supramolecular chirality. The dynamic twisting abilities of solvent molecules are often ignored and unknown, although the targeted molecules and polymers in a fluid solution are surrounded by solvent molecules. We should pay more attention to the facts that mostly all of the chemical and physical properties of these molecules and polymers in the ground and photoexcited states are significantly influenced by the surrounding solvent molecules with much conformational freedom through non-covalent supramolecular interactions between these substances and solvent molecules. This review highlights a series of studies that include: (i) historical background, covering chiral NaClO_3 crystallization in the presence of D-sugars in the late 19th century; (ii) early solvent chirality effects for optically inactive chromophores/fluorophores in the 1960s–1980s; and (iii) the recent development of mirror symmetry breaking from the corresponding achiral or optically inactive molecules and polymers with the help of molecular chirality as the solvent use quantity.

Keywords: optically active; chiral; achiral; supramolecules; polymers; solvent; circular dichroism; circularly polarized luminescence; homochirality; molecular chirality

1. Introduction

Since the late 19th century, understanding mirror symmetry breaking (MSB) has received much attention among scientists from diverse disciplines, proven by the numbers of monographs, comprehensive reviews and several original papers [1–51]. For example, the origin of biomolecular

handedness on the Earth is one of the hottest debated topics among scientists with respect to the birth of our universe and our life. Actually, except for achiral glycine, essential amino acids in proteins are L-form. All sugar moieties in DNA and RNA are D-form. The majority of scientists agree with the idea that natural selection relies on a matter of chance to induce preference; an event of spontaneous symmetry breaking. However, a minority of scientists is strongly convinced that the fundamental lack of mirror image symmetry on primordial Earth inevitably leads to the worlds of L-amino acids and D-sugars. Although it is already established that left-right symmetry is definitively broken at the elemental particle, subatomic and atomic levels [52–66], the detection of dissymmetry at the molecular level, so-called molecular parity violation (MPV), remains an unsolved issue. It is much debated whether the MPV hypothesis is valid and, even if it is true, whether it is detectable spectroscopically or by other acceptable methods [67–76].

Nevertheless, controlled mirror symmetry breaking (CMSB) might be one of the keys in the areas of organic and inorganic chemistry, supramolecular science, polymer science and materials science [77–79]. When most molecules and polymers have specific, handed stereogenic centers and/or handed stereogenic bonds, these substances become optically active or chiral. It is noted that, even if these substances are optically inactive, it does not mean that they are achiral. They may adopt a mixture of racemates or exist because of time-averaged substances in a mirror symmetric potential energy surface. It should be noted that optical activity should be recognized as an observable and/or measurable physical quantity as chiroptical signals in the ground and photoexcited states, while the definition of chirality means structural chiral substance itself, regardless of the lifetime and statistical distribution.

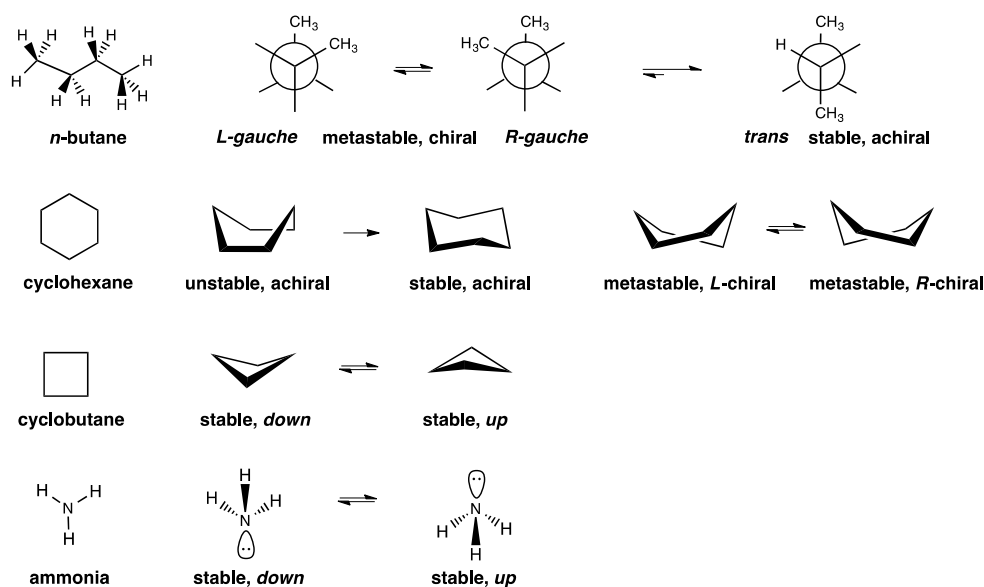
Two optically-inactive, but chirally-metastable molecules, gauche *n*-butane and twisted boat cyclohexane, and optically-inactive cyclobutane and ammonia are shown in Figure 1. *n*-Butane and cyclohexane are credited as achiral molecules. For example, *n*-butane has three rotational isomers, an enantiomeric pair of gauche forms (D_2 -symmetry, thermally metastable) and one achiral *trans* form (the most stable conformer thermally) [80,81]. Similarly, cyclohexane has two conformational achiral isomers (a stable chair and metastable boat forms) and an enantiopair of twist boats (D_2 -symmetry, metastable). However, one cannot observe any detectable optical activity of these gauche *n*-butane and twist boat cyclohexane because of their dynamic behavior, small population and ultrashort lifetime in the thermally excited states. Cyclobutane, being optically inactive and achiral, undergoes a flip-flop motion between two inversion isomers existing in a double-well minimal potential, like the ammonia molecule (Figure 1).

A possible chiral species that is detectable chiroptically is classified into two: intra- and inter-molecular origins. The former is ascribed to stereogenic centers and/or stereogenic bonds embedded in the chiral species themselves. These are ascribed on direct, straightforward chiral induction biases. The latter arises from the external influence of molecular species, including stereogenic centers and/or stereogenic bonds. These are indirect chiral induction biases. The origin of the latter is ascribed to the external influence of molecular species, including stereogenic centers and/or stereogenic bonds. These are regarded as indirect, but rather faint chiral induction biases.

With respect of the latter case, one should imagine how a target chiral/achiral molecule behaves in a liquid state: (i) a target chiral molecule is surrounded by solvent molecules; (ii) an achiral molecule is surrounded by chiral solvent molecules; (iii) a chiral molecule is surrounded by chiral solvent molecules; (iv) an achiral molecule is surrounded by achiral solvent molecules; and (v) a chiral

molecule is surrounded by chiral solvent molecules. However, although these are the faint chiral induction biases, chiral induction biases can be amplified with the help of solvent quantity. Actually, the chiroptical properties in the ground and photoexcited states of optically-inactive molecules, supramolecules and polymers are significantly affected by the surrounding solvent molecules through non-covalent supramolecular interactions between these substances and solvent molecules. The chiroptically detectable chiral species originate from a subtle balance between repulsive and attractive forces in existing chiral molecules and surrounding media.

Figure 1. Conformational isomers of *n*-butane, cyclohexane, cyclobutane and ammonia.



To detect the optical active substances in the ground states, circular dichroism (CD) and optical rotation dispersion (ORD) in electronic transition and vibrational circular dichroism and Raman optically activity in vibronic transition are useful. Contrarily, circularly polarized luminescence (CPL) allows us to detect the optical activity of chiral species in the photoexcited states. These structures are predictable computationally using the Gaussian 09 package [82–85].

This review focuses on: (i) the historical background, covering chiral NaClO_3 crystallization with sugar molecules in 1898 [4]; (ii) the early works of molecular chirality-induced MSB transfer experiments in 1960s–1990s in the presence of the solvent quantity of chiral molecules; and (iii) recent developments in solvent chirality-induced MSB from the corresponding achiral molecules, supramolecules and polymers.

2. Chiral Solvent and Chiral Additive Effects without Chemical Reactions

2.1. Optically-Active Molecules in the Ground State

In the late 19th century, Kipping and Pope reported the first successful sugar chirality transfer experiments of chiral NaClO_3 crystallization in water solutions of D-dextrose, D-mannitol and D-dulcitol [1,2,4]. In the 1960s, several workers studied the solvent chirality transfer of several small achiral and/or CD-silent molecules in isotropic solutions [86]. Mason *et al.* [87] observed for the first time an induced circular dichroism (ICD) phenomenon at forbidden *d*–*d* transitions of $[\text{Co}(\text{NH}_3)_6](\text{ClO}_4)_3$

induced by coordination with diethyl-(+)-tartrate in aqueous solution. Bosnich was the first to find ICD effects at $n-\pi$ transitions of aromatic ketones, including benzyl and benzophenone in (*S,S*)-2,3-butanediol (Figure 2) [88]. A recent vibrational experimental and *ab initio* theoretical study revealed that benzyl adopts an inherently twisting conformation due to the H–H repulsion [89]. Hayward *et al.* [90] studied the ICD effects of ten aliphatic ketones (acyclic and cyclic) in six chiral tetrahydrofuranols (Figure 2). Noack suggested the existence of a molecular complex with a 1:1 molar ratio between these ketones and L-menthol (Figure 2) [91], possibly, due to chiral OH/O interactions [92]. Many kinds of chiral alcohols are used to induce CD-active ketones in solution (Figure 3).

Figure 2. Optically-active aromatic and aliphatic ketones induced by solvent chirality.

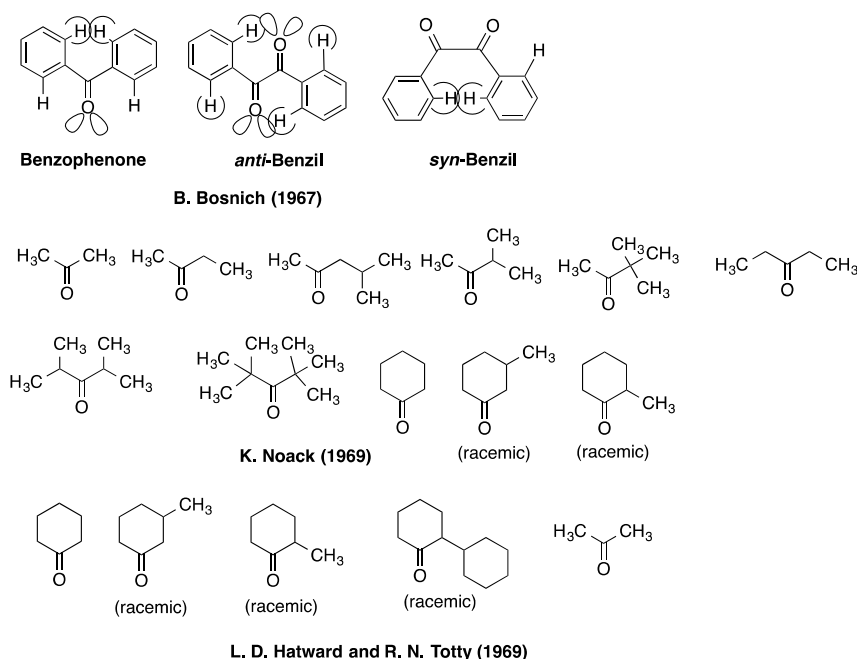
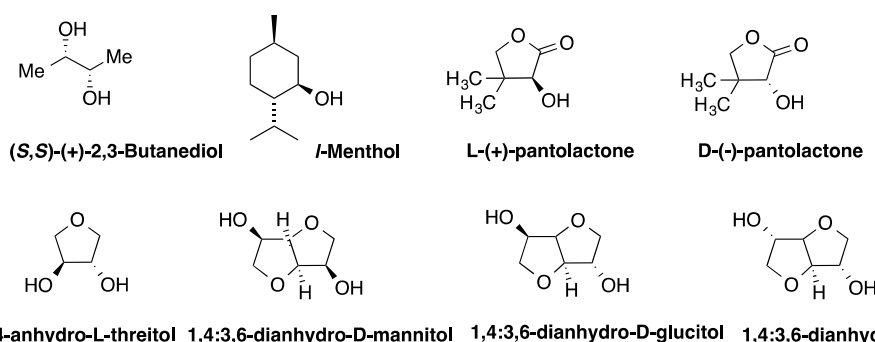


Figure 3. Chiral solvents to achiral and/or circular dichroism (CD)-silent chiral aromatic and aliphatic ketones.

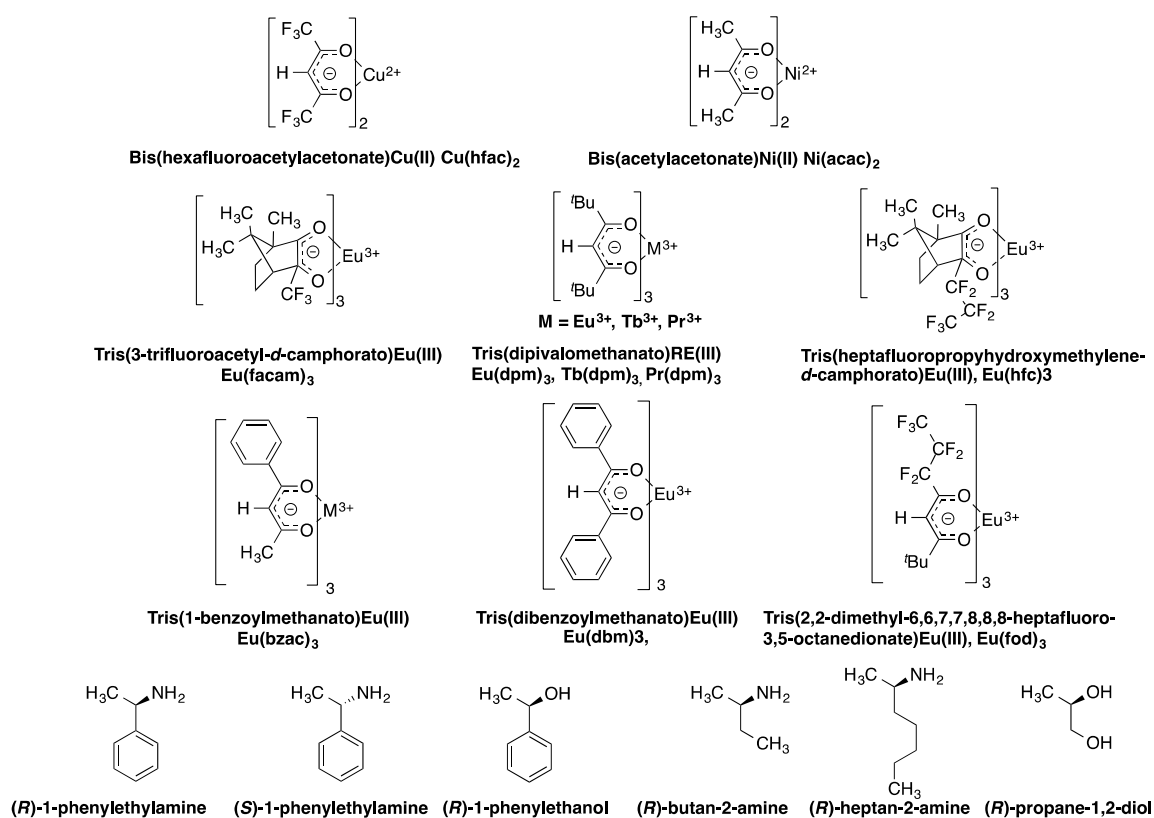


2.2. Optically Active Molecules in the Photoexcited State

In a series of studies aiming to determine the absolute stereochemical configuration of non-chromophoric alkyl alkanols, amines and more complex natural products in the UV-Vis region, Dillion and Nakanishi used optically-inactive bis(hexafluoroacetylacetonate)Cu(II) ($\text{Cu}(\text{hfac})_2$), bis(acetylacetonate)Ni(II) ($\text{Ni}(\text{acac})_2$) and tris(dipivalomethanato)Pr(III) ($\text{Pr}(\text{dpm})_3$) as molecular

chromophoric probes in the UV-visible region (Figure 4) [93–96]. Furthermore, Anderson *et al.* [97] reported CD signals from optically-inactive tris(2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedionate) Eu(III) (Eu(fod)₃) (possibly, as a mixture of Δ - and Λ -forms), known as an ¹H-NMR shift reagent, induced by various chiral 2-alkanols, 2-arylcyclohexanols, 1-phenylethylamine, amphetamine, L-menthol and a series of sesquiterpene-derived alcohols in chloroform and CCl₄ (Figure 4).

Figure 4. CD-silent, circularly polarized luminescence (CPL)-active rare-earth complexes dissolved in chiral amines and chiral alcohols; and for comparison, CD- and CPL-active Eu(hfc)₃ and Eu(facam)₃ coordinating with chiral ligands.



Aiming at absolute stereochemical configuration of non-chromophoric alkanols and alkyl amines in the UV-Vis region by CPL spectroscopy, Brittain and Richardson [98] found that, in a systematic study of the CPL characteristics of tris(3-trifluoroacetyl-*D*-camphorato)Eu(III) (Eu(facam)₃), the CPL characteristics (normalized as the g_{lum} value at two $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_2$ transitions) greatly depend on the nature of chelating solvents, including Me₂SO, DMF, a series of primary, secondary and several tertiary amines with/without dimethyl sulfoxide (Me₂SO), a series of primary, secondary and a tertiary alkanol with/without Me₂SO, a series of aliphatic ketones with/without Me₂SO and chlorinated solvents with/without Me₂SO (Figure 4). When (Eu(facam)₃) was dissolved in *tert*-butylamine, *sec*-butanol and *tert*-butanol with dimethyl sulfoxide (DMSO), the magnitude of the g_{lum} value attained ~ -2.0 , which is the theoretical limit of CPL signals. These novel results led to further reports of several CD-silent, but CPL-active β -diketonate rare-earth complexes (Eu³⁺ and Tb³⁺) dissolved in several chiral amines and chiral alcohol (Figure 4) [99,100]. Among these complexes, the g_{lum} value of Eu(dpm) dissolved in chiral aromatic amine, (*R*)-1-phenylethylamine, showed -0.5 at $^5D_0 \rightarrow ^7F_1$ transitions (594 nm), while the g_{lum} values of other Eu(fod), Eu(dbm) and Eu(bzac) in (*R*)-1-phenylethylamine

decreased to be in the order of -10^{-2} at $^5D_0 \rightarrow ^7F_1$ transitions, possibly due to overcrowded coordination between the phenyl moieties of diketonate and aromatic amine.

2.3. Optically Active Supramolecules in the Ground State

Intra- and inter-molecular CH/ π interactions, existing ubiquitously among most organic substances, have recently been established as one of the weakest hydrogen bonding interactions [98]. Aoyama *et al.* [101] designed a resorcinol cyclic tetramer bearing four long alkyl chains (host molecule) by cooperative intermolecular CH/ π interaction with various chiral alkanols (Figure 5). The host efficiently binds secondary alcohols, such as (*R*)- and (*S*)-2-pentanol and (*R*)- and (*S*)-1-phenylethanol, a tricyclic secondary alcohol (*3R*)- and (*3S*)-*endo*-tricyclo[5.2.1.0^{2,6}]deca-4,8-dien-3-ol, terpenes, such as D- and L-menthol, epimeric borneol and isoborneol and steroids, such as epicholestanol and cholesterol, characterized by CD and ¹H-NMR spectroscopies (Figure 6). The binding constant attains the order of $K = 1\text{--}54\text{ (M}^{-1}\text{)}$ at ambient temperature. However, (*S*)-limonene and L-menthyl chloride did not induce any detectable CD signals, due to the absence of OH groups in these guests.

Figure 5. Resorcinol cyclic tetramer with long alkyl chains (host). CD-silent state without chiral guests and CD-active state with the chiral guests.

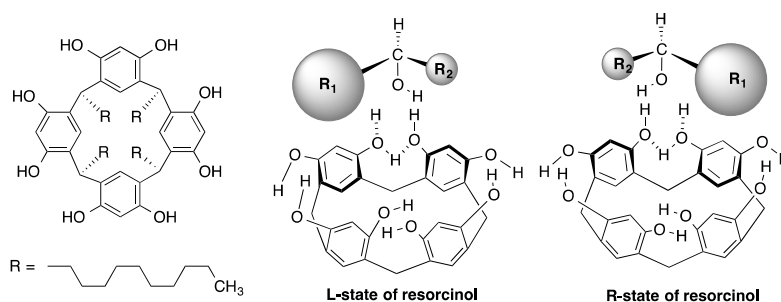
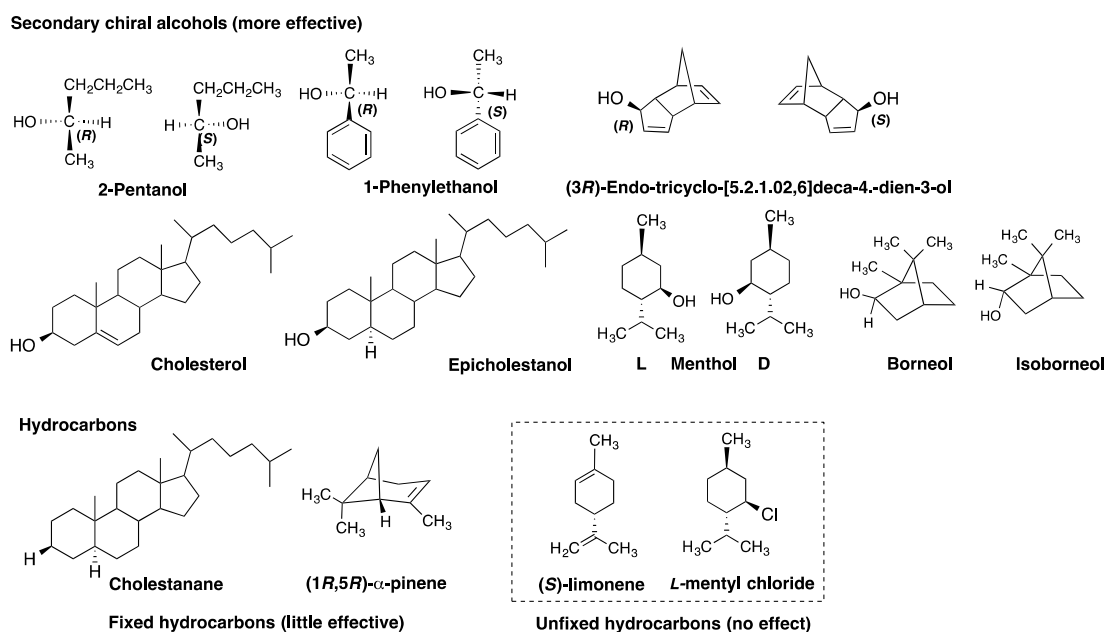


Figure 6. Chiral alcohols and hydrocarbons to induce CD-active resorcinol cyclic tetramers with L- and R-states.



Achiral CD-silent Zn bis-porphyrin linked with a flexible linker gave rise to CD-active 1:1 and 1:2 host-guest complexes with chiral amines and chiral alcohols, arising from relatively intense Zn/N and Zn/O coordination abilities. Berova, Nakanishi and coworkers [102–104] designed molecular chromophoric tweezers based on two Zn porphyrins linked with a long floppy pentamethylene diester to bind a number of chiral diamines, amino acid derivatives and amino alcohol derivatives in *n*-hexane, characterized by CD spectroscopy (Figures 7 and 8).

Figure 7. Two CD-silent Zn bis-porphyrin hosts linked with flexible linkers.

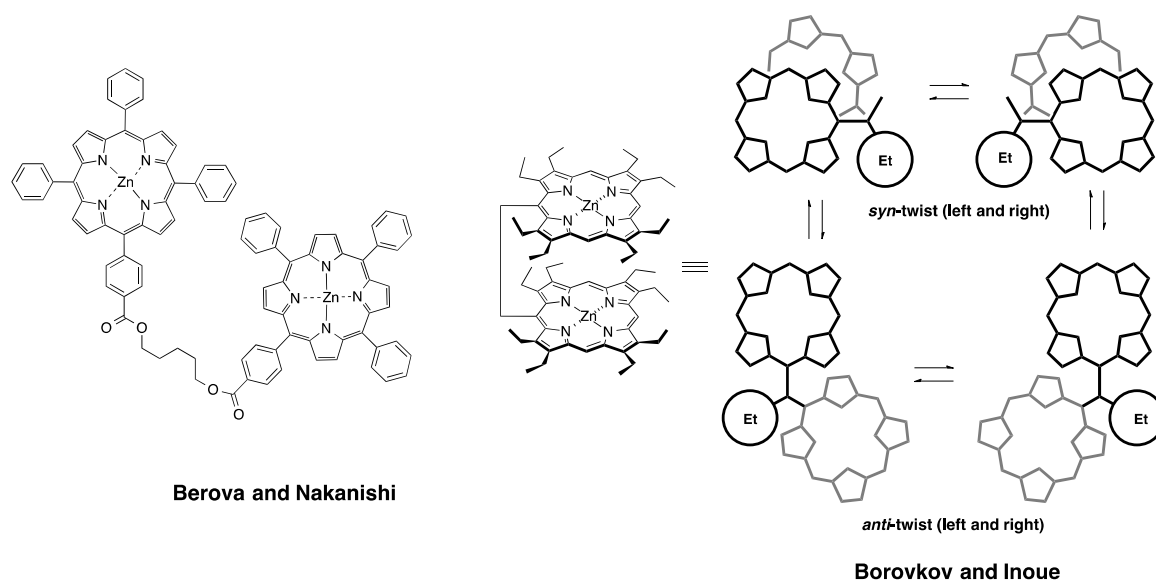
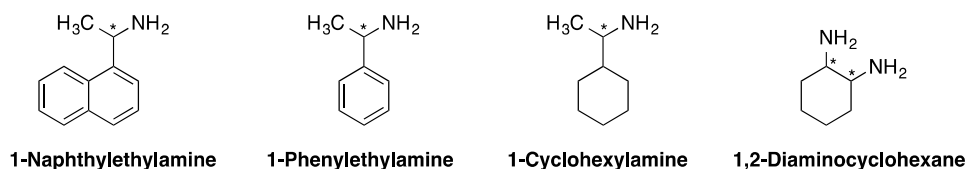


Figure 8. Chiral amine guests to induce CD-active Zn bis-porphyrins.

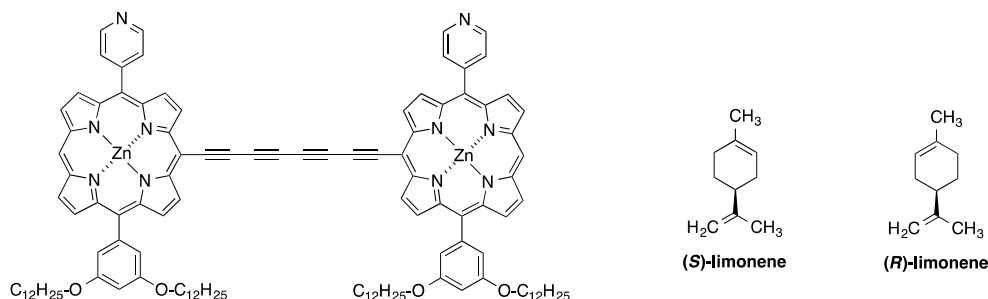


Borovkov and Inoue [105–109] showed that a twisted zinc porphyrin rotamer linked with a shorter ethane spacer can efficiently switch between *syn*- and *anti*- forms with *P*(plus)- and *M*(minus) sense by step-wise coordination with a family of chiral secondary amines and chiral secondary alcohols, proven by variable temperature UV-Vis and CD spectra and $^1\text{H-NMR}$ spectra (Figures 7 and 8). The binding constant (K) was attained in the order of 10^3 – 10^4 M^{-1} in CH_2Cl_2 , depending on the nature of the amines. The host-ligand titration curve of the Soret (B) band showed that UV-Vis and CD intensities reach a level-off at host:ligand = 1:1000 (in molar ratio). This suggested that a highly excess amount of chiral guest amines can induce chiral geometry in CD-silent dimeric porphyrin. This led us to the idea that the solvent quantity (10^0 – 10^1 M^{-1}) of chiral fluid can induce certain chiral geometry in carefully designed non-chiral hosts in double-minimal-well or multi-minimal-well potentials dissolved in fluidic condition at ambient temperature.

Actually, Aida *et al.* [110] designed a supramolecular dimeric porphyrin that is capable of forming a twisted molecular box by tetramerization dissolved in chiral hydrocarbon, (*S*)- and (*R*)-limonene through multipoint non-covalent interactions. This was proven by analyzing CD spectra at the Soret

band, as functions of limonene *ee* and the time-course CD change in a dilute condition (Figure 9).

Figure 9. A CD-silent Zn bis-porphyrin dimer that can wrap limonene molecules, leading to the corresponding tetrameric porphyrin box-encapsulated limonene.



2.4. Optically Active Polymers in the Ground State

Chiral fluidic molecules facilitate the induction of optically-active and/or helical polymers from optically-inactive, achiral and/or CD-/CPL-silent polymers with the help of van der Waals (London dispersion), CH/ π , dipole-dipole interactions in the absences of distinct intermolecular hydrogen bonding, Coulombic, charge-transfer and metal-ligand coordinating interactions.

Green *et al.* observed for the first time the generation of optically active poly(*n*-hexyl isocyanate) (PHIC) with a preferred handed helix in non-racemic solvents, such as (*S*)-1-chloro-2-methylbutane and a series of (*R*)-2-chloroalkanes, proven by CD signals (Figures 10 and 11) [111,112].

Figure 10. CD-silent poly(*n*-hexyl isocyanate).

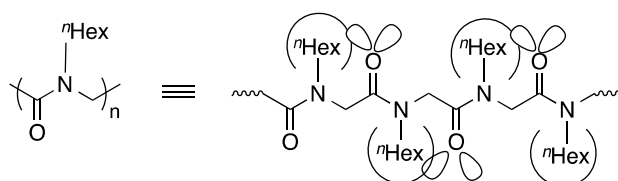
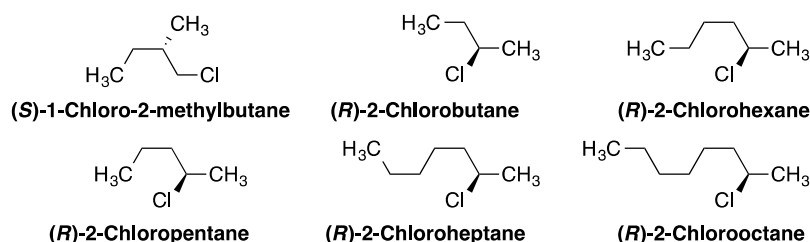
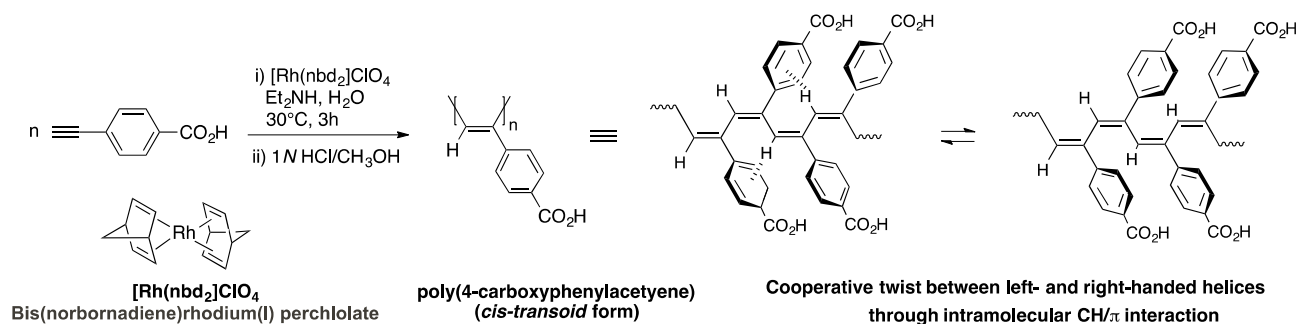
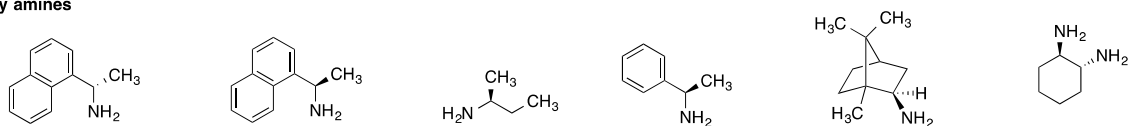


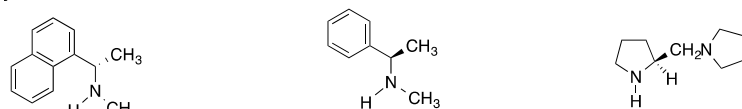
Figure 11. Chlorinate hydrocarbons enabling the induction of CD-active poly(*n*-hexyl isocyanate).



Yashima *et al.* reported generating optically-active *cis-transoid* polyphenylacetylene conveying carboxyl groups due to hydrogen bonding interactions with various chiral amines and chiral amino alcohols in polar DMSO (Figure 12) [113–115]. Optically-inactive *cis*-poly(phenylacetylene) and chiral sources (amines and amino alcohols) are dissolved in a high concentration in polar DMSO (Figures 13 and 14).

Figure 12. CD-silent poly(1-phenylacetylene) carrying carboxyl group.**Figure 13.** Chiral aliphatic and aromatic amines.**Primary amines**

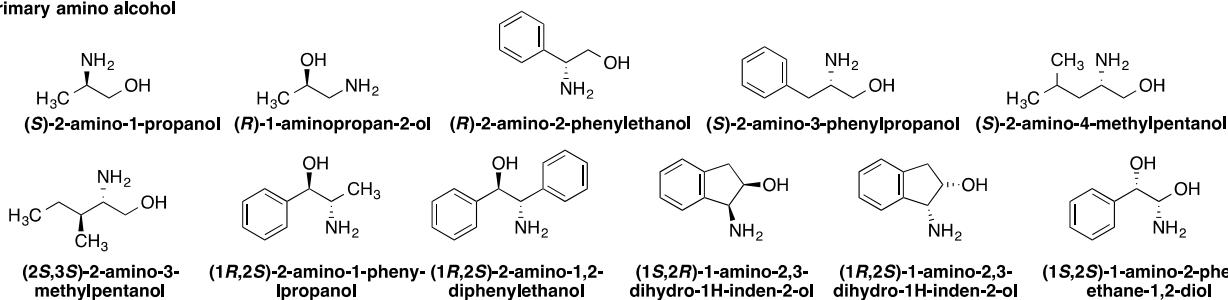
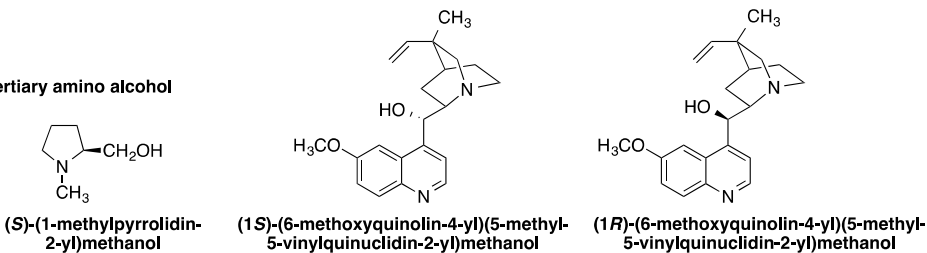
(S)-1-(1-naphthyl)ethylamine (R)-1-(1-naphthyl)ethylamine (S)-2-aminopropane (R)-1-phenylethylamine (R)-isobornylamine (1R,2R)-1,2-diaminocyclohexane

Secondary amines

(S)-N,N-dimethyl-1-(1-naphthyl)ethylamine (R)-N-methyl-1-phenylamine (S)-1-(pyrrolidin-2-ylmethyl)pyrrolidine

Tertiary amines

(R)-N,N-dimethyl-1-phenylethylamine (2R,3R)-2,3-dimethoxy-N,N,N,N-tetramethyl-1,4-diaminobutane

Figure 14. Chiral amino alcohols.**Primary amino alcohol****Tertiary amino alcohol**

2.5. Optically Active Molecular Aggregates in the Ground State

Even if chiral fluidic molecules did not induce any detectable CD signals toward optically-inactive and/or achiral molecules, these molecules often became CD-active species as a suspension in fluidic solvent(s) during aggregation process with the help of van der Waals, CH/ π , π/π stacking, dipole-dipole and hydrogen bonding interactions. Meijer *et al.* [79,115–117] demonstrated the chiroptical induction ability of terpenoids, (*S*)- and (*R*)-citronellic acid, (*S*)- and (*R*)-citronellol and (*S*)-2,6-dimethyloctane as chirality inducers to a well-defined disc-shaped molecule with C_3 symmetry and an oligophenylene bearing tri(*n*-dodecyloxy)phenyl and as one end group and a ureidotriazine moiety with multiple hydrogen-bonding ability as the other side, by cooperative π – π stacking (Figure 15). These chiral aggregations are possibly due to chiral OH/N, OH/O and CH/ π interactions upon very slow cooling (1 K per minute) confirmed by variable temperature CD spectroscopy [79,115–117]. CD-active supramolecular π – π stacks of optically-inactive guanosine derivative are formed with the help of amino acids (not solvent quantity) [118]. Optically-inactive cation-charged pyrene derivatives were generated with the help of anionic tryptophan as a chiral dopant (not solvent quantity), due to intense Coulombic interactions [119]. Recently, Würthner *et al.* [120] used naturally occurring limonene as a chiral solvent to successfully generate helical nanofiber from optically-inactive perylene bisamide derivatives carrying tri(*n*-dodecyloxy)phenyl groups, proven by variable temperature CD measurement and AFM observation (Figure 16).

Figure 15. 1,3,5-Trisubstituted benzene derivatives and oligophenylene derivatives. Chiral solvents are acyclic terpenoids derived from citronellic acids.

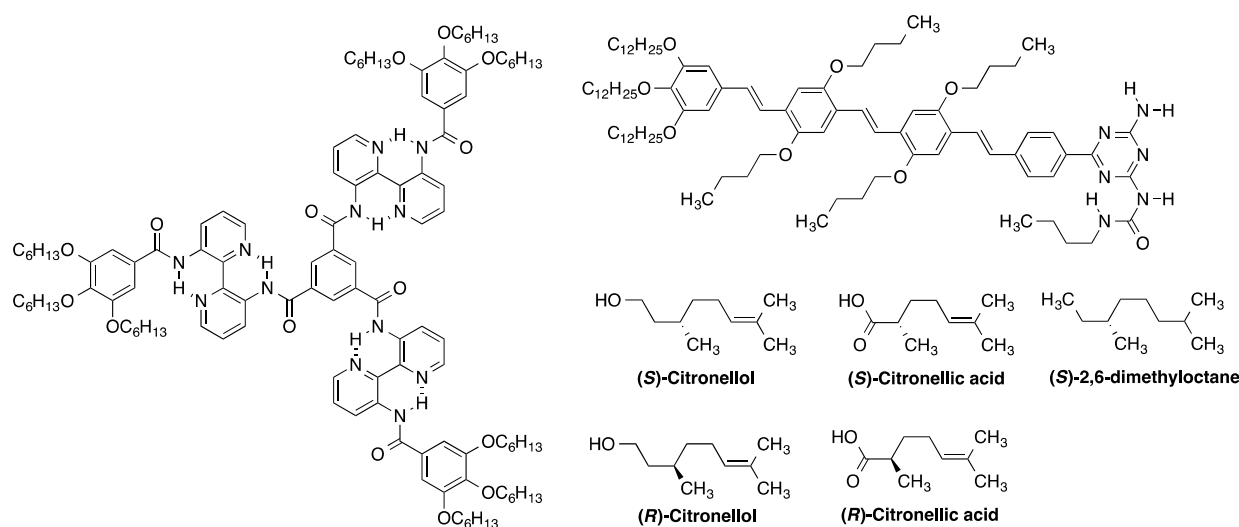
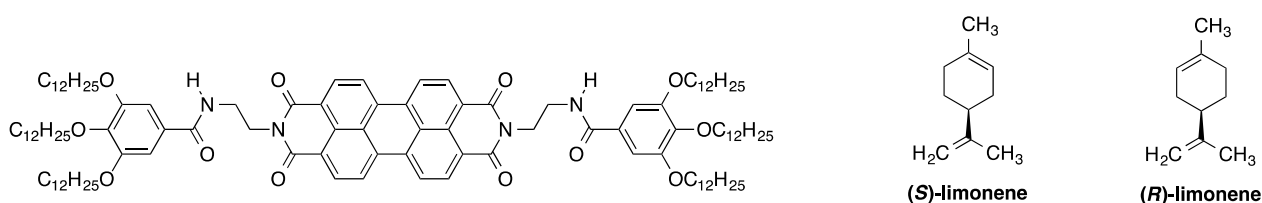


Figure 16. Perylene bisamide derivative and monocyclic terpenes, (*S*)- and (*R*)-limonenes.



2.6. Optically Active Polymer Aggregates in the Ground State

The author and coworkers have reported that a certain polysilane bearing (*S*)-2-methylbutoxyphenyl and *n*-hexyl groups dissolved in tetrahydrofuran (THF) does not show any detectable CD signals in the UV-Vis region, regardless of the presence of chiral moieties at remote positions from the Si–Si main chain (Figure 17). This polysilane is CD-silent, but abruptly revealed intense bisignate CD signals in the UV region due to the $\text{Si}\sigma\text{--Si}\sigma^*$ transition by adding methanol (aggregation-inducing poor solvent) [121]. This finding led us to the chiral solvent-induced aggregation of CD-silent polysilane bearing *n*-propoxyphenyl and *n*-hexyl groups dissolved in a mixture of toluene and methanol (Figure 17) [122]. Here, the authors used the solvent quantity of a series of chiral alcohols available commercially (Figure 18).

Figure 17. Optically active helical poly(*p*-(*S*)-2-methylbutoxyphenyl-*n*-hexylsilane) and CD-silent helical poly(*p*-*n*-propoxyphenyl-*n*-hexylsilane).

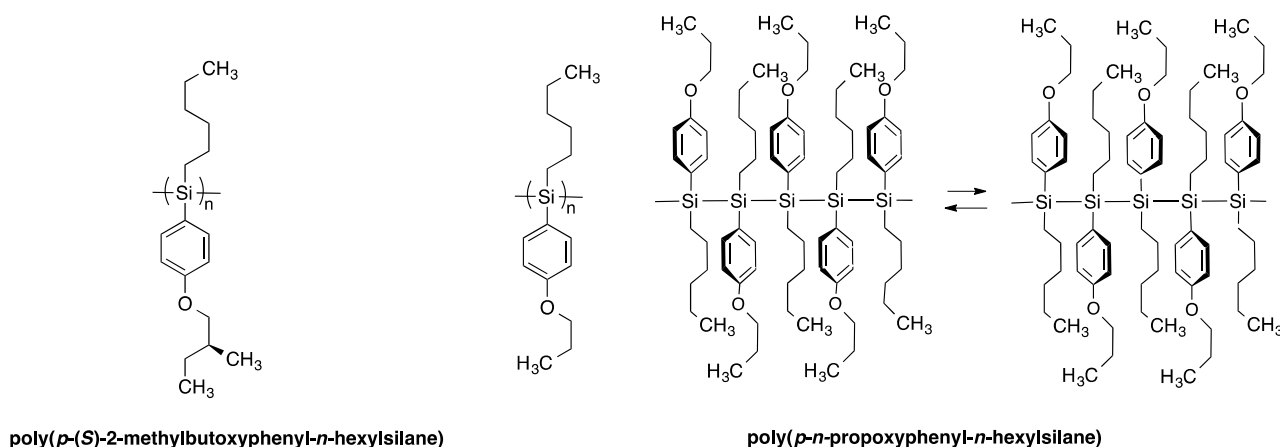
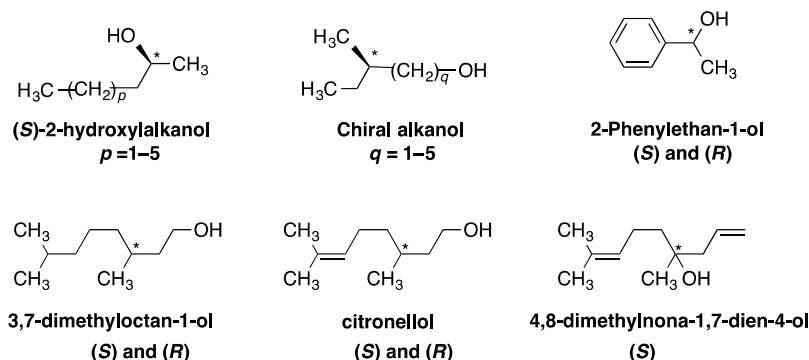


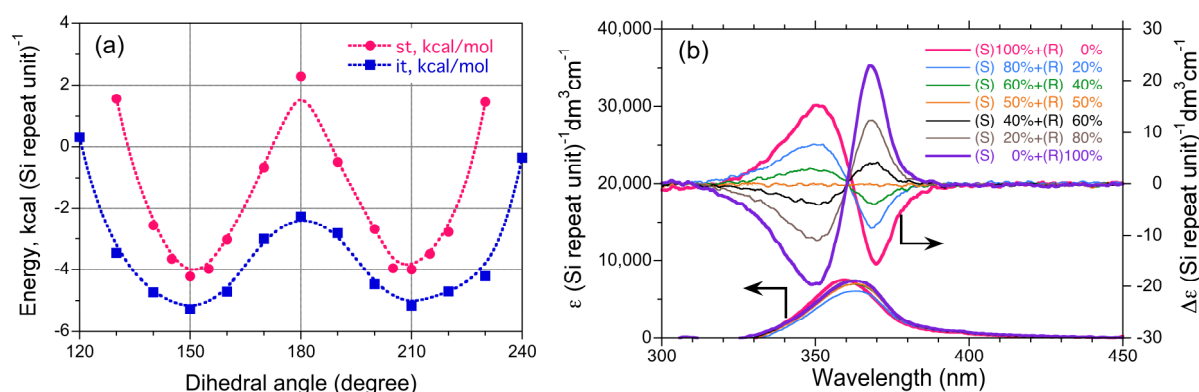
Figure 18. Optically-active alcohols as chiral solvents to generate optically active polysilane aggregates.



Our molecular mechanics (MM) calculation using the PCFF (polymer consistent force field) tuned for polymers revealed that, regardless of isotactic (*it*) and syndiotactic (*st*) sequences, the polysilane adopts a CD-silent helical conformation with an equal probability of left- and right-helices deriving from a double-well potential energy surface (Figure 19a) [121], similar to the cases of aromatic/aliphatic ketones, twisted cyclohexane, *n*-butane and cyclobutane. A possible pathway for this alcohol-induced CD originates from chiral OH/O interactions [121].

As shown in Figure 19b, the aggregates of the polysilane with *n*-propoxyphenyl and *n*-hexyl groups clearly showed exciton couplet CD signals at Si σ -Si σ^* transitions (~ 350 nm and ~ 370 nm) in response to the molecular chirality of 2-phenylethanol [121]. However, regardless of a pair of enantiopure (*S*)- and (*R*)-alcohols, we are aware that CD profiles (wavelength extrema and absolute magnitude) are exactly in non-mirror-image relation, although we did not mention this subtle difference in the original paper [121]. This non-mirror-image relation may be ascribed to some impurities, as claimed in several papers [68,71,73,117]. It may also infer other unknown reasons, such as an inherent mirror symmetry breaking at a global level upward, our universe scale [123,124] and macroscopic MPV effects [21,37,43,46,51,67,72,74].

Figure 19. (a) Potential energies of 31 mer of isotactic- and syndiotactic *p*-*n*-propoxy-phenyl-*n*-hexylsilane as a function of Si–Si dihedral angles; (b) UV-Vis and CD spectra of poly(*p*-*n*-propoxy-phenyl-*n*-hexylsilane) aggregates as a function of (*R*)- and (*S*)-2-phenylethanol (v/v). (Data adapted from [121]).



The commercially available chiral alcohols shown above are very expensive compared to common chemicals. However, this knowledge led us to the following terpene chirality transfer experiments that were successful in generating CD- and/or CPL-active π -conjugative polymer as aggregate and non-aggregate states from the corresponding CD-silent polymers existing as a racemic mixture of *P*- and *M*-helices in a double-well potential (Figure 20) [125–129]. Among several terpenes (Figure 21), nonpolar (*S*)- and (*R*)-limonenes are versatile chiral solvents that efficiently induce CD- and CPL-activity in these polymers as aggregate and non-aggregate forms, because they are inexpensive, non-toxic and recyclable liquids with a human-friendly flavor. It is worth noting that carvone and limonene oxide (a mixture of *trans* and *cis*) did not induce any detectable CD- and CPL-active polymer aggregates, possibly due to the presence of polar oxygen atoms [125,128]. However, nonpolar (*S*)- and (*R*)- α -pinenes are inducible to CD- and CPL-active polymers [126]. We assume that, similar to the non-coplanar ability of biphenyl, due to H–H repulsion (Figure 22), the inherent twisting ability between the nearest neighboring fluorene rings and between fluorene and the adjacent vinylene moiety is responsible for the double-well potential, leading to the instability of coplanar fluorene ring conformations (Figure 23) [125–128,130,131]. Indeed, fluorenes linked with a C $\equiv$ C triple bond did not produce any CD-active aggregate, due to the lack of H–H repulsion (Figure 23) [128].

Figure 20. CD-silent π -conjugated polymers as aggregates induced by solvent limonene, except for the PPA-*meta*-trialkylsilyl group and PFE.

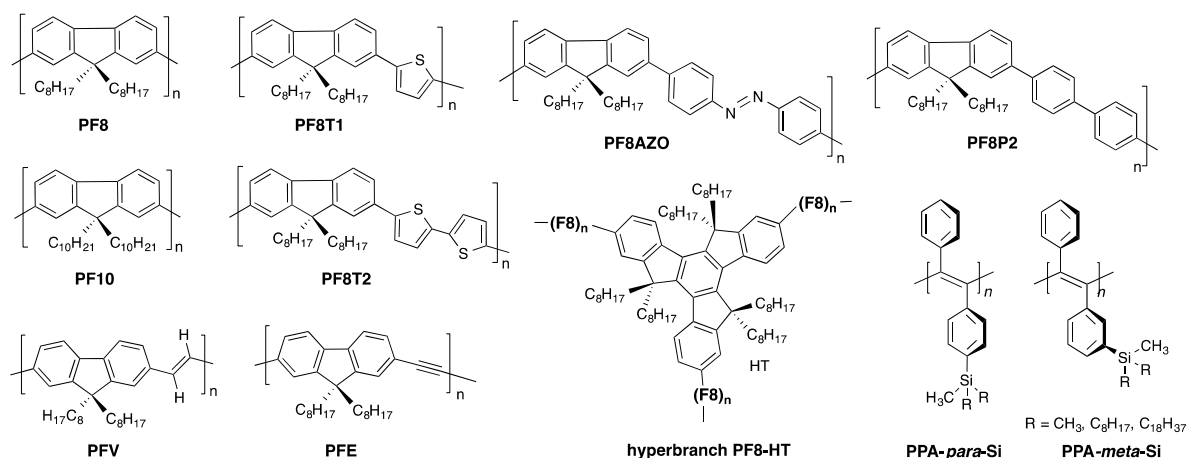


Figure 21. Chiral acyclic, monocyclic and bicyclic terpenes for studying the solvent-chirality induction ability in π - and σ -conjugated polymers.

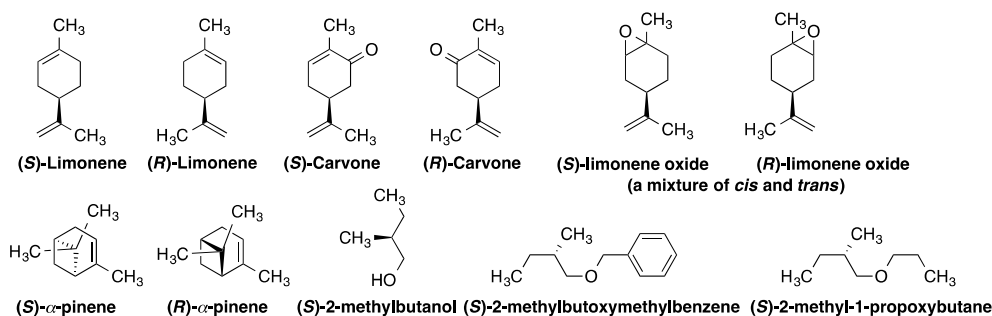


Figure 22. Inherent twisting ability of biphenyl due to the closest contact between C–H/H–C bonds.

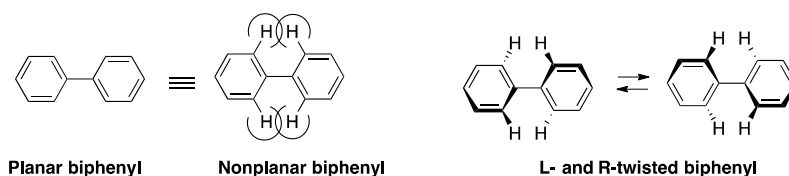
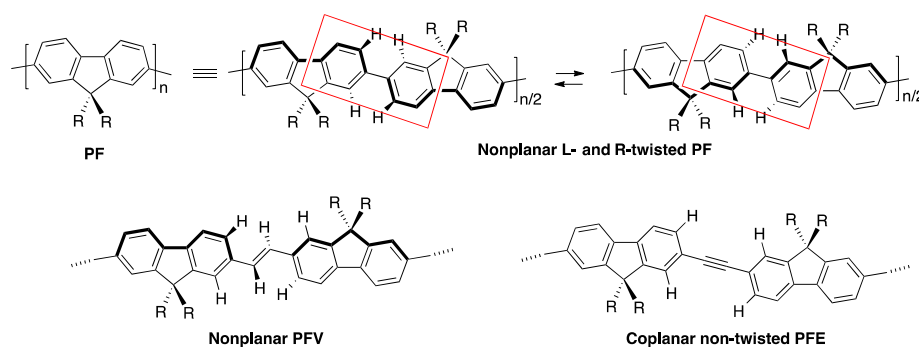


Figure 23. Inherent twisting ability with the rotational barriers of fluorene moieties in polyfluorene and poly(fluorenevinylene), due to the closest contact of the C–H/H–C bonds. For comparison, poly(fluorene-ethynylene) has no such rotational barrier.



Holder *et al.* first reported that solvent chirality transfer of two (*S*)-2-methylbutoxy derivatives without specific functional groups allows the generation of optically-active poly(methylphenylsilane) and poly(methyl-*n*-hexylsilane), which are inherently nonpolar chemical structures (Figure 24) [132,133], proven by the CD spectra. This led us to examine limonene chirality transfer aggregation in nonpolar three poly(dialkylsilane)s that are definitively in a CD-silent state in a homogeneous solution. Our MM calculation and UV absorption spectra indicated to us that three poly(dialkylsilane)s exist as a mixture of *P*-7₃ and *M*-7₃ helices [134], leading to CD- and/or CPL-silent states, as well as poly(methylphenylsilane) [133]. Recently, Akagi *et al.* showed that water-soluble poly(*p*-phenylene) bearing achiral cationic pendants turns into CD- and CPL-active spherulites suspended in mixed methanol-water (1:1 (v/v)) with the help of (*S*)- and (*R*)-binaphthols carrying anionic pendants (Figure 25) [135]. Furthermore, Campbell, Fuchter and coworkers obtained CPL- and CD-active thin films consisting of poly[(9,9-di-*n*-octylfluorenyl-2,7-diyl)-*alt*-(benzo[2,1,3]thiadiazol-4,8-diyl)] (**F8BT**), 6%–53% of 1-aza[6]helicenes by weight and 52% of [7]helicene by weight (Figure 26) [136]. If the composite films are regarded as solid solution systems, it is possible that a mixture of achiral optically-inactive and/or achiral polymers and chiral molecular solids can become CD-active and/or CPL-active solid materials.

Figure 24. CD- and/or CPL-silent polysilanes as aggregates induced by chiral solvents.

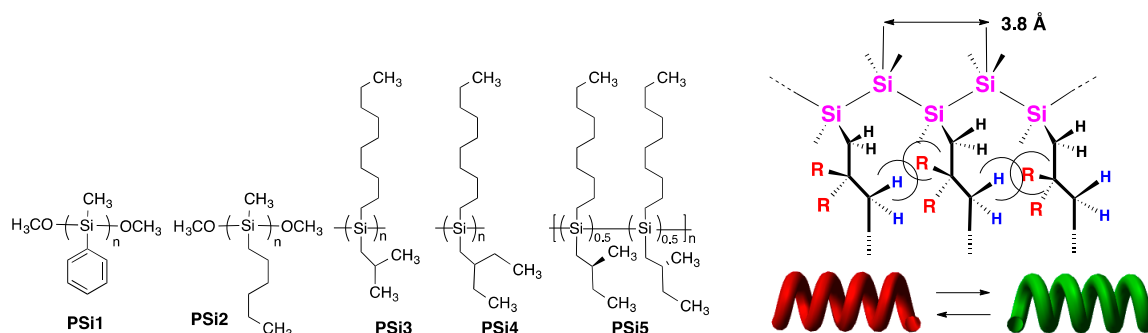


Figure 25. CD- and CPL-silent poly(*p*-phenylene) aggregates induced by chiral atropisomers.

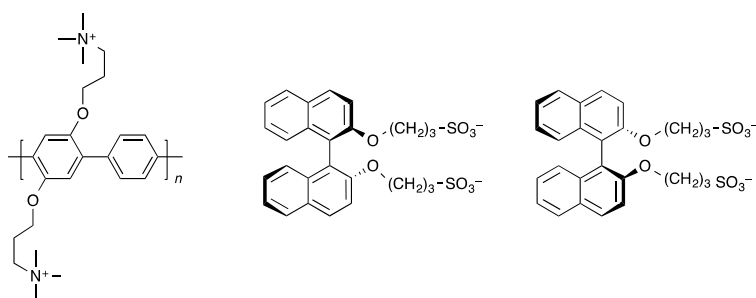
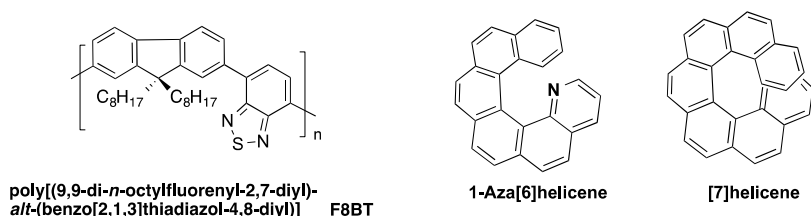


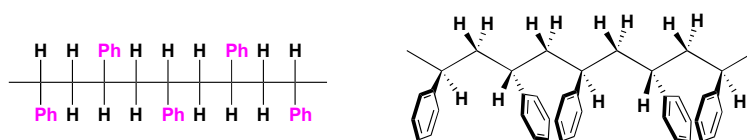
Figure 26. CD- and CPL-active **F8BT** films doped by chiral atropisomer helicene derivatives.



2.7. Optically Active Polymer Solid Crystals in the Ground State by Molecular Chirality Vapor Transfer

Molecular crystals often show polymorphs that can form several stable and metastable packing structures by containing external guest molecules into the cavity of the crystals. In 1990, Guerra *et al.* reported that syndiotactic polystyrene (s-PS) can crystallize into α , β and γ -forms depending on cooling conditions from the melt state and co-crystallize as δ and ε -forms with external host molecules (Figure 27) [137]. The same research team found that, although a δ -phase s-PS thin film becomes optically active crystals, the sign of CD signals due to the allowed π - π^* transition of phenyl rings at ≈ 200 nm is determined by the molecular chirality of the terpenes [138]. Nanoporous cavity and channels of the δ -phase are responsible for this chiral molecular sorption induced chiral crystallization. These features are characterized by CD, VCD, wide-angle-X-ray diffractometer (WAXD) and atomic force microscopy (AFM) [137–140].

Figure 27. Syndiotactic polystyrene.



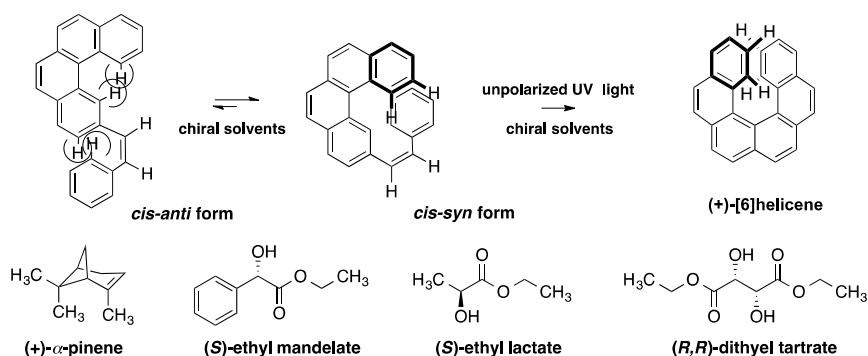
However, although they initially thought that carvone chirality determines the sign of chiral δ -phase s-PS [138] by CD spectroscopy, a more recent study refuted the previous idea and showed that the signs of CD and VCD signal δ -phase s-PS film rely on the essential nature only of the polymer host supramolecular chirality, because these chiroptical signs are not determined by carvone chirality, (*S*) or (*R*), proven by the VCD spectra of the δ -phase s-PS film used [141]. A recent VCD and theoretical study of (*R*)-limonene revealed that (*R*)-limonene has three stable rotational isomers in which the C–C bond between the isopropenyl group and equatorial cyclohexene ring can rotate freely [142]. The relative population of these three forms is approximately 1:1:1 at ambient temperature. This result should lead to the idea that δ -phase s-PS film has a function of physisorption of a certain specific rotational isomer of carvone, regardless of carvone chirality. The stereocenter of carvone is not deterministic.

3. Chiral Solvents and Chiral Additive Effects Leading to Chemical Reactions

3.1. Photochemical Cyclization

In the early 1970s, Kagan *et al.* [143,144] and Calvin *et al.* [145] independently applied a photochemical cyclization reaction—so-called absolute asymmetric synthesis—to the corresponding achiral or optically-inactive precursors in achiral solvents (benzene) by irradiating a circularly-polarized light source to synthesize non-racemic [6]helicene, but less than 1% *ee*. Dutch chemists obtained optically active [6]helicene in a range of 0.2%–2.1% *ee* by photochemically cyclizing the corresponding optically inactive precursor dissolved in several chiral solvents with the use of unpolarized light as an irradiating source (Figure 28). This uniqueness may arise from intramolecular the CH/ π interaction [146] with the help of chiral solvents [101,147].

Figure 28. Optically inactive precursor and chiral solvents for generating optically-active [6]helicene by photochemical cyclization.



3.2. Catalytic and Electrochemical Polymerization

Chiral liquid crystalline media are regarded as viscous chiral solvents able to serve as chiral influences to efficiently generate optically-active helical π -conjugated polymers. Since 1998, Akagi *et al.* have developed the chiral nematic liquid crystal field with the induced polymerization of various polymerizable monomers involving acetylene gas with the help of catalytic and electrochemical polymerization reactions (Figures 29–31) [77,148–153]. The helical shapes of polymers during polymerization are retained, because the resulting polymers are insoluble in these chiral liquid crystals.

Figure 29. Optically active *trans*- and *cis*-polyacetylene thin films generated from achiral acetylene gas, Ziegler–Natta catalyst and chiral nematic liquid crystals.

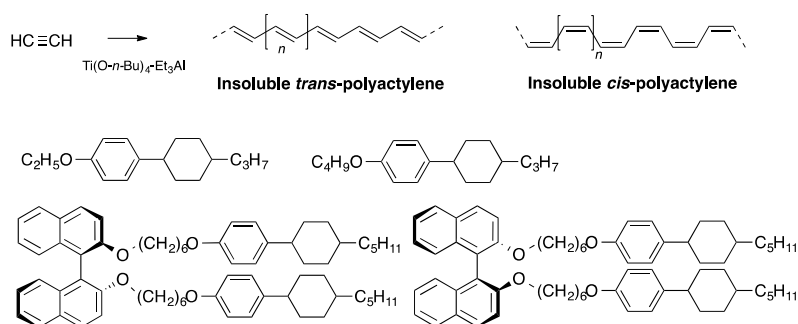


Figure 30. CD-active π -conjugated poly(bithiophene-*alt*-*p*-phenylene) film prepared by Still-coupling polymerization of the corresponding monomer in the presence of chiral nematic liquid crystals.

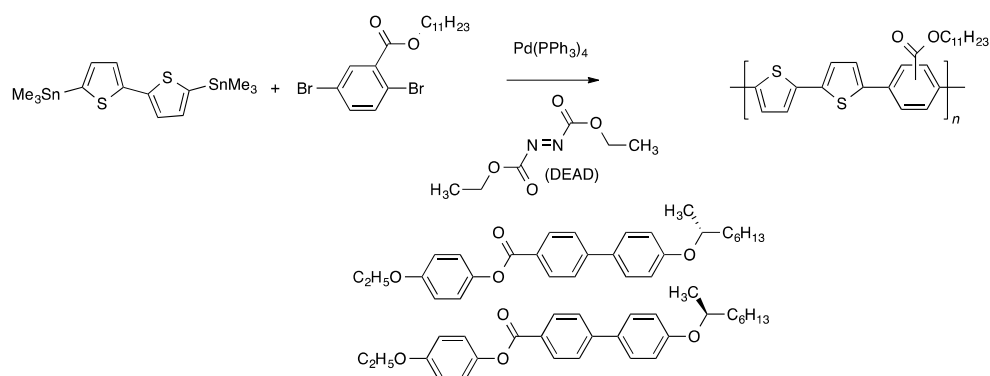
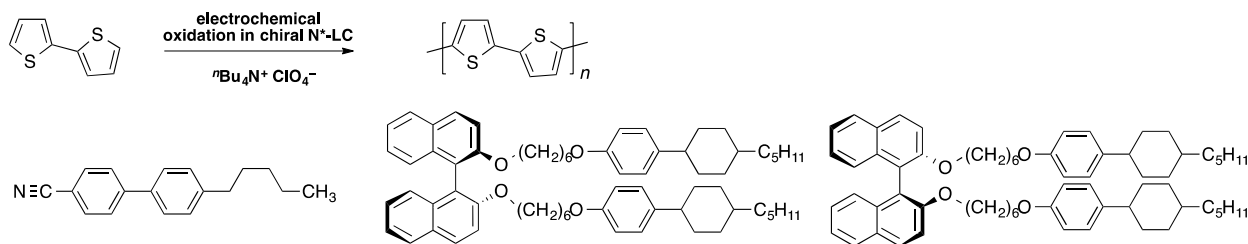


Figure 31. CD-active polythiophene films generated by electrochemical polymerization of bithiophene in the presence of chiral nematic liquid crystals and electrolyte.



Aoki *et al.* obtained CD-active helical poly(1-phenylacetylene) derivatives from the corresponding acetylene monomer carrying well-designed substituents with a hydrogen bonding ability between the nearest neighbor side chains in the presence of achiral Rhodium catalysis and chiral (*R*)-2-phenylethylamine as co-catalyst (Figure 32) [154,155]. Kwak *et al.* [156] successfully yielded optically-active *cis-cisoid* poly(diphenylacetylene)s by polymerizing achiral diphenylacetylene carrying *p*-trimethylsilylphenyl and unsubstituted phenyl groups in α -pinene with the help of achiral Rh catalyst (Figure 33). Nonpolar bicyclic rigid α -pinene was a very useful chiral solvent to efficiently provide the *cis-cisoid* poly(diphenylacetylene)s.

Figure 32. CD-active poly(1-phenylacetylene) possessing intramolecular hydrogen bonding ability prepared by catalytic (Rh(I)) polymerization of phenylacetylene with (*R*)-1-phenylethylamine.

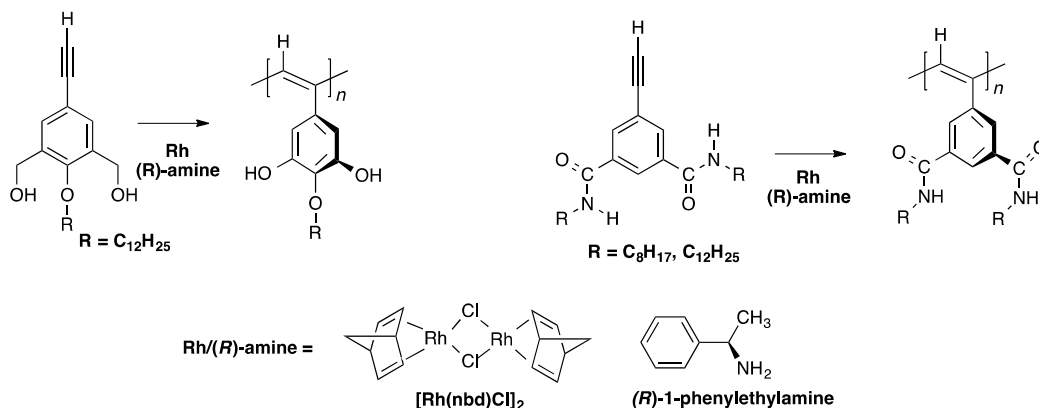
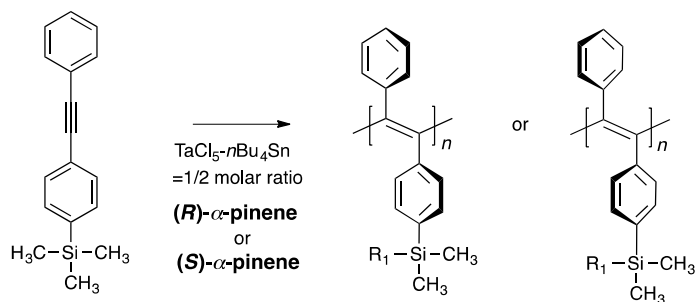


Figure 33. CD-active poly(diphenylacetylene) carrying a trimethylsilyl group at the *p*-position prepared by catalytic Ta(V)/Sn(IV) polymerization of the corresponding diphenylacetylene in solvent α -pinene.



4. Conclusions

The present review highlighted chiral solvent-induced mirror symmetry breaking of several CD-silent, CPL-silent and/or optically-inactive molecules, supramolecules and polymers in the ground and photoexcited states. It should be emphasized that we always imagine the dynamic behaviors of twisting and/or flip-flop motions of optically-inactive molecules, supramolecules and polymers surrounded by fluidic solvent molecules and the existence of non-covalent interactions between these substances. Most chemical and physical properties of these molecules and polymers in the ground and photoexcited states might be influenced by chiral molecules, due to much conformational freedom. These invisible interactions between these chiral solvents and optically inactive substances are possible to spectroscopically visualize with the help of CD, CPL, ORD and VCD spectra, as well as computational prediction.

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Conflicts of Interest

The author declares no conflict of interest.

References

1. Kipping, F.S.; Pope, W.J. Racemism and pseudoracemism. *J. Chem. Soc.* **1897**, 71, 989–1001.
2. Kipping, F.S.; Pope, W.J. Enantiomorphism. *J. Chem. Soc.* **1898**, 73, 606–617.
3. Japp, F.R. Stereochemistry and Vitalism. *Nature* **1898**, 58, 54–55.
4. Kipping, F.; Pope, W.J. The crystallisation of externally compensated mixtures. *J. Chem. Soc. Trans.* **1909**, 95, 103–108.
5. Frank, F.C. On spontaneous asymmetric synthesis. *Biochim. Biophys. Acta* **1953**, 11, 459–463.
6. Wald, G. The origin of optical activity. *Ann. N. Y. Acad. Sci.* **1957**, 69, 352–368.
7. Ulbricht, T.L.V.; Vester, F. Attempts to induce optical activity with polarized β -radiation. *Tetrahedron* **1962**, 18, 629–637.
8. Yamagata, Y. A hypothesis for the asymmetric appearance of biomolecules on earth. *J. Theor. Biol.* **1966**, 11, 495–498.
9. Thiemann, W.; Darge, W. Experimental attempts for the study of the origin of optical activity on earth. *Orig. Life* **1974**, 5, 263–283.
10. Rein, D. Some remarks on parity violating effects of intramolecular interactions. *J. Mol. Evol.* **1974**, 4, 15–22.
11. Letokhov, V.S. On difference of energy levels of left and right molecules due to weak interactions. *Phys. Lett.* **1975**, 53A, 275–276.

12. Zel'dovich, B.Y.; Saakyan, D.B.; Sobel'man, I.I. Energy difference between right- and left-hand molecules, due to parity nonconservation in weak interactions of electrons with nuclei. *Sov. Phys. JETP Lett.* **1977**, *25*, 94–97.
13. Keszthelyi, L. Origin of the asymmetry of biomolecules and weak interaction. *Orig. Life* **1977**, *8*, 299–340.
14. Harris, R.A.; Stodolsky, L. Quantum beats in optical activity and weak interactions. *Phys. Lett.* **1978**, *78B*, 313–317.
15. Hegstrom, R.A.; Rein, D.W.; Sandars, P.G.H. Calculation of the parity nonconserving energy difference between mirror-image molecules. *J. Chem. Phys.* **1980**, *73*, 2329–2341.
16. Mason, S.F. Origins of biomolecular handedness. *Nature* **1984**, *311*, 19–23.
17. Hegstrom, R.A. Weak neutral current and β radiolysis effects on the origin of the biomolecular chirality. *Nature* **1985**, *315*, 749–750.
18. Kondepudi, D.K.; Nelson, G.W. Weak neutral currents and the origin of biomolecular chirality. *Nature* **1985**, *314*, 438–441.
19. Mason, S.F.; Tranter, G.E. The electroweak origin of biomolecular handedness. *Proc. R. Soc. Lond. A* **1985**, *A397*, 45–65.
20. Quack, M. On the measurement of the parity violating energy difference between enantiomers. *Chem. Phys. Lett.* **1986**, *132*, 147–153.
21. Barron, L.D. Symmetry and molecular chirality. *Chem. Soc. Rev.* **1986**, *15*, 189–223.
22. Applequist, J. Optical activity: Biot's bequest. *Am. Sci.* **1987**, *75*, 59–68.
23. Wiesenfeld, L. Effect of atomic number on parity-violating energy differences between enantiomers, O, S, Se, Te. *Mol. Phys.* **1988**, *64*, 739–745.
24. Gardner, M. *The New Ambidextrous Universe—Symmetry and Asymmetry from Mirror Reflections to Superstrings*, 3rd ed.; Freeman: New York, NY, USA, 1990.
25. Barra, A.L.; Robert, J.B.; Wiesenfeld, L. Possible observation of parity nonconservation by high-resolution NMR. *Europhys. Lett.* **1988**, *5*, 217–222.
26. Avetisov, V.A.; Goldanskii, V.I.; Kuz'min, V.V. Handedness, origin of life and evolution. *Phys. Today* **1991**, *44*, 33–41.
27. Latel, H. Parity Violation in Atomic Physics. In *Chirality—From Weak Bosons to the α -Helix*; Janoschek, R., Ed.; Springer: Berlin, Germany, 1992; Chapter 1, pp. 1–17.
28. Bonner, W.A. The origin and amplification of biomolecular chirality. *Orig. Life Evol. Biosph.* **1991**, *21*, 59–111.
29. Salam, A. The role of chirality in the origin of life. *J. Mol. Evol.* **1991**, *33*, 105–113.
30. Orgel, L. Molecular replication. *Nature* **1992**, *358*, 203–209.
31. Kikuchi, O.; Kiyonaga, H. Parity-violating energy shift of helical *n*-alkane. *J. Mol. Struct.* **1994**, *312*, 271–274.
32. Bada, J.L. Origins of homochirality. *Nature* **1995**, *374*, 594–595.
33. Cline, D.B. *Physical Origin of Homochirality in Life*; AIP Conference Proceedings Series 379; AIP Press: Woodbury, NY, USA, 1996.
34. Avalos, M.; Babiano, R.; Cintas, P.; Jiménez, J.; Palacios, J.; Barron, L.D. Absolute asymmetric synthesis under physical fields: Facts and fictions. *Chem. Rev.* **1998**, *98*, 2845–2874.

35. Bailey, J.; Chrysostomou, A.; Hough, J.H.; Gledhill, T.M.; McCall, A.; Clark, S.; Ménard, F.; Tamura, M. Circular polarization in star-formation regions: Implications for biomolecular homochirality. *Science* **1998**, *281*, 672–674.
36. Laerdahl, J.; Schwerdtfeger, P. Fully relativistic *ab initio* calculations of the energies of chiral molecules including parity-violating weak interactions. *Phys. Rev. A* **1999**, *60*, 4439–4450.
37. Szabó-Nagy, A.; Keszthelyi, L. Demonstration of the parity-violating energy difference between enantiomers. *Proc. Natl. Acad. Sci. USA* **1999**, *96*, 4252–4255.
38. Feringa, B.L.; van Delden, R.A. Absolute asymmetric synthesis: The origin, control, and amplification of chirality. *Angew. Chem. Int. Ed.* **1999**, *38*, 3418–3438.
39. Avalos, M.; Babiano, R.; Cintas, P.; Jiménez, J.; Palacios, J. From parity to chirality: Chemical implications revisited. *Tetrahedron Asymmetry* **2000**, *11*, 2991–2404.
40. MacDermott, A.J. The ascent of parity-violation: Exochirality in the solar system and beyond. *Enantiomer* **2000**, *5*, 153–168.
41. Avalos, M.; Babiano, R.; Cintas, P.; Jiménez, J.L.; Palacios, J.C. Chiral autocatalysis: Where stereochemistry meets the origin of life. *Chem. Commun.* **2000**, 887–892.
42. Frank, P.; Bonner, W.A.; Zare, R. On One Hand But Not the Other: The Challenge of the Origin and Survival of Homochirality in Prebiotic Chemistry. In *Chemistry for the 21st Century*; Keinan, E., Schechter, E., Eds.; Wiley-VCH: Weinheim, Germany, 2001; Chapter 11, pp. 175–208.
43. Fujiki, M. Experimental tests of parity violation at helical polysilylene level. *Macromol. Rapid Commun.* **2001**, *22*, 669–674.
44. Lough, L.W.; Wainer, I.W. *Chirality in Natural and Applied Science*; Blackwell: Oxford, UK, 2002.
45. Quack, M. How important is parity violation for molecular and biomolecular chirality? *Angew. Chem. Int. Ed.* **2002**, *41*, 4618–4630.
46. Shinitzky, M.; Nudelman, F.; Barda, Y.; Haimovitz, R.; Chen, E.; Deamer, D.W. Unexpected differences between D- and L-tyrosine lead to chiral enhancement in racemic mixtures. *Orig. Life Evol. Biosph.* **2002**, *32*, 285–297.
47. Crassous, J.; Chardonnet, C.; Saue, T.; Schwerdtfeger, P. Recent experimental and theoretical developments towards the observation of parity violation (PV) effects in molecules by spectroscopy. *Org. Biomol. Chem.* **2005**, *3*, 2218–2224.
48. Wagnière, G.H. *On Chirality and the Universal Asymmetry—Reflections in Image and Mirror Image*; Wiley-VCH: Weinheim, Germany, 2007.
49. Soai, K.; Kawasaki, T. Asymmetric autocatalysis with amplification of chirality. *Top. Curr. Chem.* **2008**, *284*, 1–33.
50. Guijarro, A.; Yus, M. *The Origin of Chirality in the Molecules of Life*; RSC: London, UK, 2009.
51. Fujiki, M. Mirror symmetry breaking in helical polysilanes: Preference between left and right of chemical and physical origin. *Symmetry* **2010**, *2*, 1625–1652.
52. Lee, T.D.; Yang, C.N. Question of parity conservation in weak interactions. *Phys. Rev.* **1956**, *105*, 254–258.
53. Wu, C.S.; Ambler, E.; Hayward, R.W.; Hoppes, D.D.; Hudson, R.P. Experimental test of parity conservation in beta decay. *Phys. Rev.* **1957**, *105*, 1413–1415.

54. Nambu, Y.; Jona-Lasinio, G. Dynamical model of elementary particles based on an analogy with Superconductivity. I. *Phys. Rev.* **1961**, *122*, 345–358.
55. Nambu, Y.; Jona-Lasinio, G. Dynamical model of elementary particles based on an analogy with superconductivity. II. *Phys. Rev.* **1961**, *124*, 246–254.
56. Cabibbo, N. Unitary symmetry and leptonic decays. *Phys. Rev. Lett.* **1963**, *10*, 531–533.
57. Wigner, E.P. Violations of symmetry in physics. *Sci. Am.* **1965**, *213*, 28–36.
58. Kobayashi, M.; Maskawa, T. CP-Violation in the renormalizable theory of weak interaction. *Prog. Theor. Phys.* **1973**, *49*, 652–657.
59. Weinberg, S. Conceptual foundations of the unified theory of weak and electromagnetic interactions. *Rev. Mod. Phys.* **1980**, *52*, 515–523.
60. Salam, A. Gauge unification of fundamental forces. *Rev. Mod. Phys.* **1980**, *52*, 525–538.
61. Glashow, S.L. Towards a unified theory: Threads in a tapestry. *Rev. Mod. Phys.* **1980**, *52*, 539–543.
62. Rubbia, C. Experimental observation of the intermediate vector bosons W^+ , W^- , and Z^0 . *Rev. Mod. Phys.* **1985**, *57*, 699–722.
63. Bouchiat, M.-A.; Pottier, L. Optical experiments and weak interactions. *Science* **1986**, *234*, 1203–1210.
64. Adair, R.K. A flaw in a universal mirror. *Sci. Am.* **1988**, *258*, 30–36.
65. Sozzi, M.S. *Discrete Symmetries and CP Violation: From Experiment to Theory*; Oxford University Press: Oxford, UK, 2008.
66. Frois, B.; Bouchiat, M.-A. *Parity Violation in Atoms and Polarized Electron Scattering*; World Scientific: London, UK, 1999.
67. Wang, W.; Yi, F.; Ni, Y.; Zhao, Z.; Jin, X.; Tang, Y. Parity violation of electroweak force in phase transitions of single crystals of D- and L-alanine and valine. *J. Biol. Phys.* **2000**, *26*, 51–65.
68. Sullivan, R.; Pyda, M.; Pak, J.; Wunderlich, B.; Thompson, J.R.; Pagni, R.; Pan, H.; Barnes, C.; Schwerdtfeger, P.; Compton, R. Search for electroweak interactions in amino acid crystals. II. The Salam hypothesis. *J. Phys. Chem. A* **2003**, *107*, 6674–6680.
69. Laubender, G.; Berger, R. *Ab initio* calculation of parity-violating chemical shifts in NMR spectra of chiral molecules. *ChemPhysChem* **2003**, *4*, 395–399.
70. Weijs, V.; Manninen, P.; Vaara, J. Perturbational calculations of parity-violating effects in nuclear-magnetic-resonance parameters. *J. Chem. Phys.* **2005**, *123*, doi:10.1063/1.1961321.
71. Wilson, C.C.; Myles, D.; Ghosh, M.; Johnson, L.N.; Wang, W. Neutron diffraction investigations of L- and D-alanine at different temperatures: The search for structural evidence for parity violation. *New J. Chem.* **2005**, *29*, 1318–1322.
72. Scolnik, Y.; Portnaya, I.; Cogan, U.; Tal, S.; Haimovitz, R.; Fridkin, M.; Elitzur, A.C.; Deamer, D.W.; Shinitzky, M. Subtle differences in structural transitions between poly-L- and poly-D-amino acids of equal length in water. *Phys. Chem. Chem. Phys.* **2006**, *8*, 333–339.
73. Lahav, M.; Weissbuch, I.; Shavit, E.; Reiner, C.; Nicholson, G.J.; Schurig, V. Parity violating energetic difference and enantiomorphous crystals-caveats; Reinvestigation of tyrosine crystallization. *Orig. Life Evol. Biosph.* **2006**, *36*, 151–170.
74. Kodona, E.K.; Alexopoulos, C.; Panou-Pomonis, E.; Pomonis, P.J. Chirality and helix stability of polyglutamic acid enantiomers. *J. Colloid Interface Sci.* **2008**, *319*, 72–80.

75. Figgen, D.; Schwerdtfeger, P. Structures, inversion barriers, and parity violation effects in chiral SeOXY molecules (X,Y = H, F, Cl, Br, or I). *J. Chem. Phys.* **2009**, *130*, doi:10.1063/1.3072370.
76. Darquié, B.; Stoeffler, C.; Shelkovnikov, A.; Daussey, C.; Amy-Klein, A.; Chardonnet, C.; Zrig, S.; Guy, L.; Crassous, J.; Soulard, P.; *et al.* Progress toward the first observation of parity violation in chiral molecules by high-resolution laser spectroscopy. *Chirality* **2010**, *22*, 870–884.
77. Akagi, K. Helical polyacetylene: Asymmetric polymerization in a chiral liquid-crystal field. *Chem. Rev.* **2009**, *109*, 5354–5401.
78. Yashima, E.; Maeda, K.; Iida, H.; Furusho, Y.; Nagai, K. Helical polymers: Synthesis, structures, and functions. *Chem. Rev.* **2009**, *109*, 6102–6211.
79. De Greef, T.F.A.; Smulders, M.M.J.; Wolffs, M.; Schenning, A.P.H.J.; Sijbesma, R.P.; Meijer, E.W. Supramolecular Polymerization. *Chem. Rev.* **2009**, *109*, 5687–5754.
80. Vollhardt, K.P.C.; Schore, N.E. *Organic Chemistry: Structure and Function*, 6th ed.; Freeman: New York, NY, USA, 2010.
81. Juaristi, E. *Introduction to Stereochemistry & Conformational Analysis*; Wiley-Interscience: New York, NY, USA, 1991.
82. Berova, N.; Polavarapu, P.L.; Nakanishi, K.; Woody, R.W. *Comprehensive Chiroptical Spectroscopy—Instrumentation, Methodologies, and Theoretical Simulations*; Wiley: New York, NY, USA, 2012.
83. Riehl, J.P.; Richardson, F.S. Circularly polarized luminescence spectroscopy. *Chem. Rev.* **1986**, *86*, 1–16.
84. Dekkers, H.P.J.M. Circularly Polarized Luminescence: A Probe for Chirality in the Excited State. In *Circular Dichroism: Principles and Applications*, 2nd ed.; Berova, N., Nakanishi, K., Woody, R.W., Eds.; Wiley-VCH: New York, NY, USA, 2000; Chapter 7.
85. Frisch, M.J.; Trucks, G.W.; Schlegel, H.B.; Scuseria, G.E.; Robb, M.A.; Cheeseman, J.R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G.A.; *et al.* *Gaussian 09*; Gaussian, Inc.: Wallingford, CT, USA, 2013.
86. Hatano, M. *Induced Circular Dichroisms in Biopolymer-Dye Systems*; Springer: Heidelberg, Germany, 1986.
87. Mason, S.F.; Norman, B.J. Outer-sphere co-ordination and optical activity in transition-metal complexes. *Chem. Commun.* **1965**, 335–336.
88. Bosnich, B. Asymmetric syntheses, asymmetric transformations, and asymmetric inductions in an optically active solvent. *J. Am. Chem. Soc.* **1967**, *89*, 6143–6148.
89. Bezrodnaya, T.V.; Mel'nik, V.I.; Puchkovskaya, G.A.; Savranskii, L.I. Vibrational and electronic spectra of benzophenone in different phase states: *Ab initio* calculations and experiment. *J. Struct. Chem.* **2006**, *47*, 194–199.
90. Hayward, L.D.; Totty, R.N. Induced optical rotation and circular dichroism of symmetric and racemic aliphatic carbonyl compounds. *J. Chem. Soc. D. Chem. Commun.* **1969**, 676–677.
91. Noack, K. Circular dichroism induction in an optically inactive compound by intermolecular interaction with an optically active solvent. *Helv. Chim. Acta* **1969**, *52*, 2501–2507.
92. Desiraju, G.R.; Steiner, T. *The Weak Hydrogen Bond in Structural Chemistry and Biology*; Oxford University Press: Oxford, UK, 1999.

93. Dillion, J.; Nakanishi, K. Use of copper hexafluoroacetylacetonate for the determination of the absolute configuration of alcohols. *J. Am. Chem. Soc.* **1974**, *96*, 4055–4057.
94. Dillion, J.; Nakanishi, K. Use of complexing agents for determining the absolute configurations of α -glycols and α -amino alcohols. Basic systems. *J. Am. Chem. Soc.* **1974**, *96*, 4057–4059.
95. Dillion, J.; Nakanishi, K. Use of complexing agents for determining the absolute configurations of α -glycols and α -amino alcohols. Applications to complex natural products. *J. Am. Chem. Soc.* **1974**, *96*, 4059–4061.
96. Dillion, J.; Nakanishi, K. Absolute configurational studies of vicinal glycols and amino alcohols. II. With $\text{Pr}(\text{dpm})_3$. *J. Am. Chem. Soc.* **1975**, *97*, 5417–5422.
97. Andersen, N.H.; Bottino, B.J.; Moore, A.; Shaw, J.R. Metal ion probes of molecular geometry. II. A direct spectroscopic determination of the absolute configuration of hydroxyl bearing asymmetric centers based on the shift reagent, $\text{Eu}(\text{FOD})$. *J. Am. Chem. Soc.* **1974**, *96*, 603–604.
98. Brittain, H.G.; Richardson, F.S. Circularly polarized emission studies on the chiral nuclear magnetic resonance lanthanide shift reagent tris(3-trifluoroacetyl-D-camphorato)europium(III). *J. Am. Chem. Soc.* **1976**, *98*, 5858–5863.
99. Brittain, H.G.; Richardson, F.S. Circularly polarized emission studies on chiral and achiral europium(III) β -diketonate complexes in an optically active solvent. *J. Am. Chem. Soc.* **1976**, *99*, 65–70.
100. Brittain, H.G. Correlation of circularly polarized luminescence induced in $\text{Tb}(\text{dpm})_3$ by chiral solvents with the absolute configuration of those solvents. *J. Am. Chem. Soc.* **1980**, *102*, 1207–1280.
101. Kobayashi, K.; Asakawa, Y.; Kikuchi, Y.; Toi, H.; Aoyama, Y. $\text{CH}-\pi$ interaction as an important driving force of host-guest complexation in apolar organic media. Binding of monools and acetylated compounds to resorcinol cyclic tetramer as studied by proton NMR and circular dichroism spectroscopy. *J. Am. Chem. Soc.* **1993**, *115*, 2648–2654.
102. Huang, X.; Rickman, B.H.; Borhan, B.; Berova, N.; Nakanishi, K. Zinc porphyrin tweezer in host-guest complexation: Determination of absolute configurations of diamines, amino acids, and amino alcohols by circular dichroism. *J. Am. Chem. Soc.* **1998**, *120*, 6185–6186.
103. Kurtán, T.; Nesnas, N.; Li, Y.-Q.; Huang, X.; Nakanishi, K.; Berova, N. Chiral recognition by CD-sensitive dimeric zinc porphyrin host. 1. Chiroptical protocol for absolute configurational assignments of monoalcohols and primary monoamines. *J. Am. Chem. Soc.* **2001**, *123*, 5962–5973.
104. Kurtán, T.; Nesnas, N.; Koehn, F.E.; Li, Y.-Q.; Nakanishi, K.; Berova, N. Chiral recognition by CD-sensitive dimeric zinc porphyrin host. 2. Structural studies of host-guest complexes with chiral alcohol and monoamine conjugates. *J. Am. Chem. Soc.* **2001**, *123*, 5974–5982.
105. Borovkov, V.V.; Lintuluoto, J.M.; Sugeta, H.; Fujiki, M.; Arakawa, R.; Inoue, Y. Supramolecular chirogenesis in zinc porphyrins: Equilibria, binding properties, and thermodynamics. *J. Am. Chem. Soc.* **2002**, *124*, 2993–3006.
106. Borovkov, V.V.; Hembury, G.A.; Inoue, Y. The origin of solvent-controlled supramolecular chirality switching in a bis(zinc porphyrin) system. *Angew. Chem. Int. Ed.* **2003**, *42*, 5310–5314.
107. Borovkov, V.V.; Hembury, G.A.; Yamamoto, N.; Inoue, Y. Supramolecular chirogenesis in zinc porphyrins: Investigation of zinc-freebase bis-porphyrin, new mechanistic insights, extension of sensing abilities, and solvent effect. *J. Phys. Chem. A* **2003**, *107*, 8677–8686.

108. Borovkov, V.V.; Fujii, I.; Muranaka, A.; Hembury, G.A.; Tanaka, T.; Ceulemans, A.; Kobayashi, N.; Inoue, Y. Rationalization of supramolecular chirality in a bisporphyrin system. *Angew. Chem. Int. Ed.* **2004**, *116*, 5597–5601.
109. Borovkov, V. Supramolecular chirality in porphyrin chemistry. *Symmetry* **2014**, *6*, 256–294.
110. Aimi, J.; Oya, K.; Tsuda, A.; Aida, T. Chiroptical sensing of asymmetric hydrocarbons using a homochiral supramolecular box from a bismetallporphyrin rotamer. *Angew. Chem. Int. Ed.* **2007**, *46*, 2031–2035.
111. Green, M.M.; Khatri, C.; Peterson, N.C. A macromolecular conformational change driven by a minute chiral solvation energy. *J. Am. Chem. Soc.* **1993**, *115*, 4941–4942.
112. Green, M.M.; Park, J.-W.; Sato, T.; Teramoto, A.; Lifson, S.; Robin L.B.; Selinger, R.L.B.; Selinger, J.V. The macromolecular route to chiral amplification. *Angew. Chem. Int. Ed.* **1999**, *38*, 3138–3154.
113. Yashima, E.; Matsushima, T.; Okamoto, Y. Poly((4-carboxyphenyl)acetylene) as a probe for chirality assignment of amines by circular dichroism. *J. Am. Chem. Soc.* **1995**, *117*, 11596–11597.
114. Yashima, E.; Maeda, K.; Okamoto, Y. Memory of macromolecular helicity assisted by interaction with achiral small molecules. *Nature* **1999**, *399*, 449–451.
115. Palmans, A.R.A.; Vekemans, J.A.J.M.; Havinga, E.E.; Meijer, E.W. Sergeants-and-soldiers principle in chiral columnar stacks of disc-shaped molecules with C₃ symmetry. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2648–2651.
116. George, S.J.; Tomović, Z.; Smulders, M.M.J.; de Greef, T.F.A.; Leclère, P.E.L.G.; Meijer, E.W.; Schenning, A.P.H.J. Helicity induction and amplification in an oligo(*p*-phenylenevinylene) assembly through hydrogen-bonded chiral acids. *Angew. Chem. Int. Ed.* **2007**, *46*, 8206–8211.
117. George, S.J.; Tomović, Z.; Schenning, A.P.H.J.; Meijer, E.W. Insight into the chiral induction in supramolecular stacks through preferential chiral solvation. *Chem. Commun.* **2011**, *47*, 3451–3453.
118. Fenniri, H.; Deng, B.-L.; Ribbe, A.E. Helical rosette nanotubes with tunable chiroptical properties. *J. Am. Chem. Soc.* **2002**, *124*, 11064–11072.
119. Xiao, J.; Xu, J.; Cui, S.; Liu, H.; Wang, S.; Li, Y. Supramolecular helix of an amphiphilic pyrene derivative induced by chiral tryptophan through electrostatic interactions. *Org. Lett.* **2008**, *10*, 645–648.
120. Stepanenko, V.; Li, X.Q.; Gershberg, J.; Würthner, F. Evidence for kinetic nucleation in helical nanofiber formation directed by chiral solvent for a perylene bisimide organogelator. *Chem. Eur. J.* **2013**, *19*, 4176–4183.
121. Nakashima, H.; Fujiki, M.; Koe, J.R.; Motonaga, M. Solvent and temperature effects on the chiral aggregation of poly(alkylarylsilane)s bearing remote chiral groups. *J. Am. Chem. Soc.* **2001**, *123*, 1963–1969.
122. Nakashima, H.; Koe, J.R.; Torimitsu, K.; Fujiki, M. Transfer and amplification of chiral molecular information to polysilylene aggregates. *J. Am. Chem. Soc.* **2001**, *123*, 4847–4848.
123. Shinitzky, M. Space asymmetry as a possible global feature. *Chirality* **2013**, *25*, 308–311.
124. Pavlov, V.V.; Klabunovskii, E.I. Homochirality origin in nature: Possible versions. *Curr. Org. Chem.* **2014**, *18*, 93–114.

125. Kawagoe, Y.; Fujiki, M.; Nakano, Y. Limonene magic: Noncovalent molecular chirality transfer leading to ambidextrous circularly polarised luminescent π -conjugated polymers. *New J. Chem.* **2010**, *34*, 637–647.
126. Nakano, Y.; Liu, Y.; Fujiki, M. Ambidextrous circular dichroism and circularly polarised luminescence from poly(9,9-di-*n*-decylfluorene) by terpene chirality transfer. *Polym. Chem.* **2010**, *1*, 460–469.
127. Zhang, W.; Yoshida, K.; Fujiki, M.; Zhu, X. Unpolarized-light-driven amplified chiroptical modulation between chiral aggregation and achiral disaggregation of an azobenzene-*alt*-fluorene copolymer in limonene. *Macromolecules* **2011**, *44*, 5105–5111.
128. Fujiki, M.; Jalilah, A.J.; Suzuki, N.; Taguchi, M.; Zhang, W.; Abdellatif, M.M.; Nomura, K. Chiral optofluidics: Gigantic circularly polarized light enhancement of *all-trans*-poly(9,9-di-*n*-octylfluorene-2,7-vinylene) during mirror-symmetry-breaking aggregation by optically tuning fluidic media. *RSC Adv.* **2012**, *2*, 6663–6671.
129. Lee, D.; Jin, Y.-J.; Suzuki, N.; Fujiki, M.; Sakaguchi, T.; Kim, S.; Lee, W.-E.; Kwak, G. Solvent-to-polymer chirality transfer in intramolecular stack structure. *Macromolecules* **2012**, *45*, 5379–5386.
130. Fujiki, M.; Kawagoe, Y.; Nakano, Y.; Nakao, A. Mirror-symmetry-breaking in poly[(9,9-di-*n*-octylfluorenyl-2,7-diyl)-*alt*-biphenyl] (PF8P2) is susceptible to terpene chirality, achiral solvents, and mechanical stirring. *Molecules* **2013**, *18*, 7035–7057.
131. Liu, J.; Zhang, J.; Zhang, S.; Suzuki, N.; Fujiki, M.; Wang, L.; Li, L.; Zhang, W.; Zhou, N.; Zhu, X. Chiroptical generation and amplification of hyperbranched π -conjugated polymers in aggregation states driven by limonene chirality. *Polym. Chem.* **2014**, *5*, 784–791.
132. Dellaportas, P.; Jones, R.G.; Holder, S.J. Induction of preferential helical screw senses in optically inactive polysilanes via chiral solvation. *Macromol. Rapid Commun.* **2002**, *23*, 99–103.
133. Toyoda, S.; Fujiki, M. Cooperative preferential helical ordering in poly(alkylarylsilylene) copolymers. *Macromolecules* **2001**, *34*, 640–644.
134. Nakano, Y.; Ichiyanagi, F.; Naito, M.; Yang, Y.; Fujiki, M. Chiroptical generation and inversion during the mirror-symmetry-breaking aggregation of dialkylpolysilanes due to limonene chirality. *Chem. Commun.* **2012**, *48*, 6636–6638.
135. Watanabe, K.; Iida, H.; Akagi, K. Circularly polarized blue luminescent spherulites consisting of hierarchically assembled ionic conjugated polymers with a helically π -stacked structure. *Adv. Mater.* **2012**, *24*, 6451–6456.
136. Yang, Y.; da Costa, R.C.; Smilgies, D.-M.; Campbell, A.J.; Fuchter, M.J. Induction of circularly polarized electroluminescence from an achiral light-Emitting polymer via a chiral small-molecule dopant. *Adv. Mater.* **2013**, *25*, 2624–2628.
137. Guerra, G.; Vitagliano, V.M.; de Rosa, C.; Petraccone, V.; Corradini, P. Polymorphism in melt crystallized syndiotactic polystyrene samples. *Macromolecules* **1990**, *23*, 1539–1544.
138. Buono, A.M.; Immediata, I.; Rizzo, P.; Guerra, G. Detection and memory of nonracemic molecules by a racemic host polymer film. *J. Am. Chem. Soc.* **2007**, *129*, 10992–10993.
139. Guadagno, L.; Raimondo, M.; Silvestre, C.; Immediata, I.; Rizzoc, P.; Guerra, G. Processing, thermal stability and morphology of chiral sensing syndiotactic polystyrene films. *J. Mater. Chem.* **2008**, *18*, 567–572.

140. Rizzo, P.; Beltrani, M.; Guerra, G. Induced vibrational circular dichroism and polymorphism of syndiotactic polystyrene. *Chirality* **2010**, *22*, E67–E73.
141. Rizzo, P.; Lepera, E.; Guerra, G. Enantiomeric guests with the same signs of chiral optical responses. *Chem. Commun.* **2014**, *50*, 8185–8188.
142. Ureña, F.P.; Moreno, J.R.A.; González, J.J.L. Conformational study of (*R*)-(+)-limonene in the liquid phase using vibrational spectroscopy (IR, Raman, and VCD) and DFT calculations. *Tetrahedron Asymmetry* **2009**, *20*, 89–97.
143. Moradpour, A.; Nicoud, J.F.; Balavoine, G.; Kagan, H.; Tsoucaris, G. Photochemistry with circularly polarized light. Synthesis of optically active hexahelicene. *J. Am. Chem. Soc.* **1971**, *93*, 2353–2354.
144. Kagan, H.; Moradpour, A.; Nicoud, J.F.; Balavoine, G.; Martin, R.H.; Cosyn, J.P. Photochemistry with circularly polarised light. II. asymmetric synthesis of octa and nonahelicene. *Tetrahedron Lett.* **1971**, *27*, 2479–2482.
145. Bernstein, W.J.; Calvin, M.; Buchardt, O. Absolute asymmetric synthesis. I. Mechanism of the photochemical synthesis of nonracemic helixenes with circularly polarized light. wavelength dependence of the optical yield of octahelicene. *J. Am. Chem. Soc.* **1972**, *94*, 494–498.
146. Takahashi, O.; Kohno, Y.; Nishio, M. Relevance of weak hydrogen bonds in the conformation of organic compounds and bioconjugates: Evidence from recent experimental data and high-level ab initio MO calculations. *Chem. Rev.* **2010**, *110*, 6049–6076.
147. Laarhoven, W.H.; Cuppen, T.J.H.M. Chiral solvent-induced asymmetric synthesis; photosynthesis of optically enriched hexahelicene. *J. Chem. Soc. Chem. Commun.* **1977**, doi:10.1039/C3977000047A.
148. Akagi, K.; Piao, G.; Kaneko, S.; Sakamaki, K.; Shirakawa, H.; Kyotani, M. Helical polyacetylene synthesized with a chiral nematic reaction field. *Science* **1998**, *282*, 1683–1686.
149. Goto, H.; Akagi, K. Optically active conjugated polymers prepared from achiral monomers by polycondensation in a chiral nematic solvent. *Angew. Chem. Int. Ed.* **2005**, *44*, 4322–4328.
150. Goto, H.; Akagi, K. Asymmetric electrochemical polymerization: Preparation of polybithiophene in a chiral nematic liquid crystal field and optically active electrochromism. *Macromolecules* **2005**, *38*, 1091–1098.
151. Matsushita, S.; Kyotani, M.; Akagi, K. Hierarchically controlled helical graphite films prepared from iodine-doped helical polyacetylene films using morphology-retaining carbonization. *J. Am. Chem. Soc.* **2011**, *133*, 17977–17992.
152. San Jose, B.A.; Matsushita, S.; Akagi, K. Lyotropic chiral nematic liquid crystalline aliphatic conjugated polymers based on disubstituted polyacetylene derivatives that exhibit high dissymmetry factors in circularly polarized luminescence. *J. Am. Chem. Soc.* **2012**, *134*, 19795–19807.
153. Park, J.; Goh, M.; Akagi, K. Helical nylons and polyphthalamides synthesized by chiral interfacial polymerizations between chiral nematic liquid crystal and water layers. *Macromolecules* **2014**, *47*, 2784–2795.
154. Aoki, T.; Kaneko, T.; Maruyama, N.; Sumi, A.; Takahashi, M.; Sato, T.; Teraguchi, M. Helix-sense-selective polymerization of phenylacetylene having two hydroxy groups using a chiral catalytic system. *J. Am. Chem. Soc.* **2003**, *125*, 6346–6347.

155. Teraguchi, M.; Tanioka, D.; Kaneko, T.; Aoki, T. Helix-sense-selective polymerization of achiral phenylacetylenes with two N-alkylamide groups to generate the one-handed helical polymers stabilized by intramolecular hydrogen bonds. *ACS Macro Lett.* **2012**, *1*, 1258–1261.
156. Kim, H.; Lee, D.; Lee, S.; Suzuki, N.; Fujiki, M.; Lee, C.-L.; Kwak, G. Optically active conjugated polymer from solvent chirality transfer polymerization in monoterpenes. *Macromol. Rapid Commun.* **2013**, *34*, 1471–1479.

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