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# Chiroptical Polymer Functionalized by Chiral Nanofibrillar Network

*Hiroataka Ihara, Makoto Takafuji and Yutaka Kuwahara*

## Abstract

Chirality is one of the basic factors that influence a wide range of activities from chemical synthesis to tissue construction in life phenomena. Recently, researchers have attempted to use chirality as an optical signal. In animals, it is used to transmit information to insects and crustaceans, and it has also been confirmed that it promotes growth in plants. This chapter presents a new organic system that produces a chiral optical signal, that is, circularly polarized luminescence (CPL), which has been attracting attention in recent years. In particular, the chapter is focused on the generating CPL through chirality induction with the chiral self-assembling phenomenon and explaining its application as an optical film.

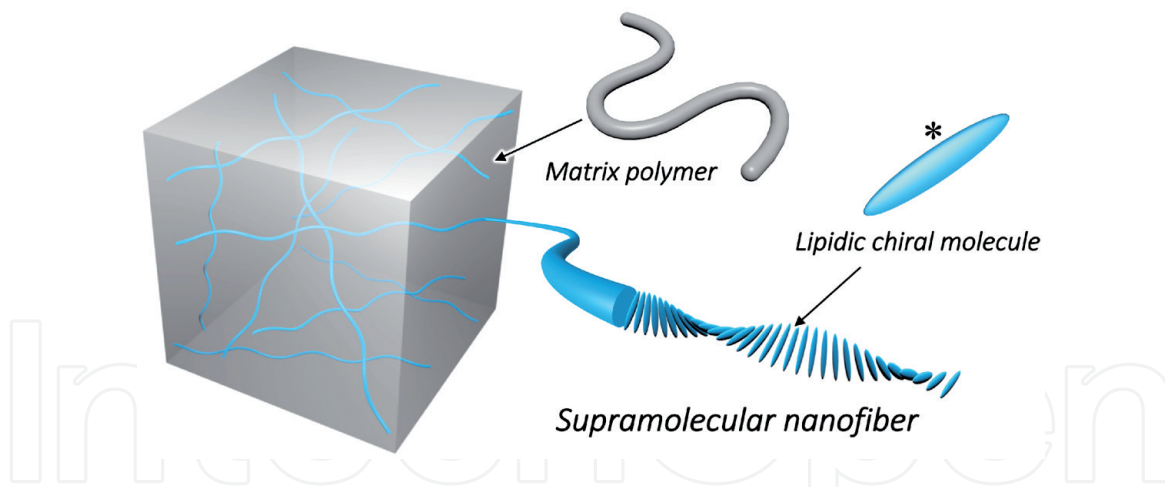
**Keywords:** self-assembling, supramolecular gel, nanofibril, circular dichroism, circularly polarized luminescence

## 1. Introduction

Fiber materials have applications in various industrial fields. One of these is compounding with bulk polymer materials to improve and strengthen their physical strength by controlling factors such as the bending elastic modulus, tensile strength, and thermal expansion coefficient. Generally, the higher the dispersion of fibers in polymer, the higher the effect on polymer.

Typical examples of fibers with industrial applications are carbon fibers, aramid fibers, and whiskers. In recent years, cellulose nanofibers [1] having a nano-sized diameter have attracted attention not only because they can be manufactured using inexhaustible and inexpensive raw materials but also because the strength of each cellulose nanofiber is 1/5th that of iron and 5 times the strength [2, 3]. Therefore, if the process cost and the method of dispersion of cellulose nanofibers in bulk materials can be improved and established, it will be used in various materials and fields, such as automobiles and home appliances.

In this chapter, we focus on the low light-scattering property due to the sufficiently small diameters as optical materials because transparency is one of the most important physical elements. Inorganic glass is a transparent material with excellent heat resistance, light resistance, and chemical resistance. Therefore, it is almost universally used as a partition plate during material conversion and energy conversion using light as an energy source. However, inorganic glass is heavy, inflexible, and fragile, and to improve impact resistance, laminated glass with an organic polymer as an interlayer film is often used. Therefore, there is a need for



**Figure 1.**  
A strategic approach to highly functionalizing polymer materials through self-assembled growth into nanofibers.

a transparent material that is light, soft, and has good processability. Transparent polymers are suitable to replace glass because organic polymers are essentially light at the elemental level and can be adjusted for hardness and flexibility. In addition, it is attractive that expansive functionality can be tailor-made at the monomer level.

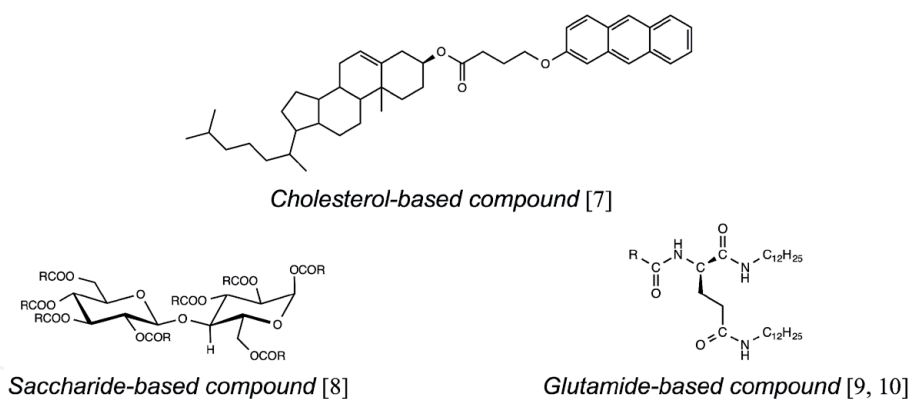
One of the methods for imparting functions while taking advantage of such characteristics of organic polymers is to blend fillers. This method is particularly applicable to general-purpose polymers and is widely used for function enhancement and function conversion. Among them, nano-sized fillers are attracting particular attention in applications that require transparency because they have low light-scattering properties. However, there are several challenges in the use of nanofillers, and at present, reducing process costs and simplifying the compounding process are the main focus issues. In particular, simplification of the compounding process is a universal problem that results from the high specific surface area of nanomaterials and is thus often a barrier to development and research. This problem also exists in the cellulose nanofibers mentioned above.

This chapter outlines an approach (**Figure 1**) that utilizes nanofiber formation [4–6] using the self-assembly of small molecules as a new strategic method for functionalizing polymer materials; also, an example of its application as an optical material is introduced.

## 2. Opt functional nanofibers by self-assembly

While various methods for creating nanofibers have been developed, it is difficult to unravel a mass of nanofibers once entangled by a process that is complicated and requires high energy. A typical example is cellulose nanofibers (CNFs). CNFs are environmentally friendly and have excellent potential functions; therefore, ensuring efficient dispersion of CNFs is essential to develop their applications. The method introduced in this chapter is not used for unraveling entangled nanofibers, but rather a for growing nanofibers in a bulk polymer (**Figure 1**). Therefore, because the material used is a low-molecular-weight organic substance, a nanofiber-forming material that is structurally compatible with the polymer material can be selected. This approach promises a surfactant-free process in compounding polymeric materials.

To grow nanofibers in polymers, we utilize self-assembling gelation, which is a novel method in solution systems. Well-known molecular materials for this purpose are cholesterol derivatives [7], sugar derivatives [8], and amino acid derivatives [9, 10] (**Figure 2**). These materials associate in a self-organizing manner by promoting weak



**Figure 2.**

Compounds that cause a molecular gelation phenomenon due to the formation of nanofiber-like aggregates by self-assembling [7–10].

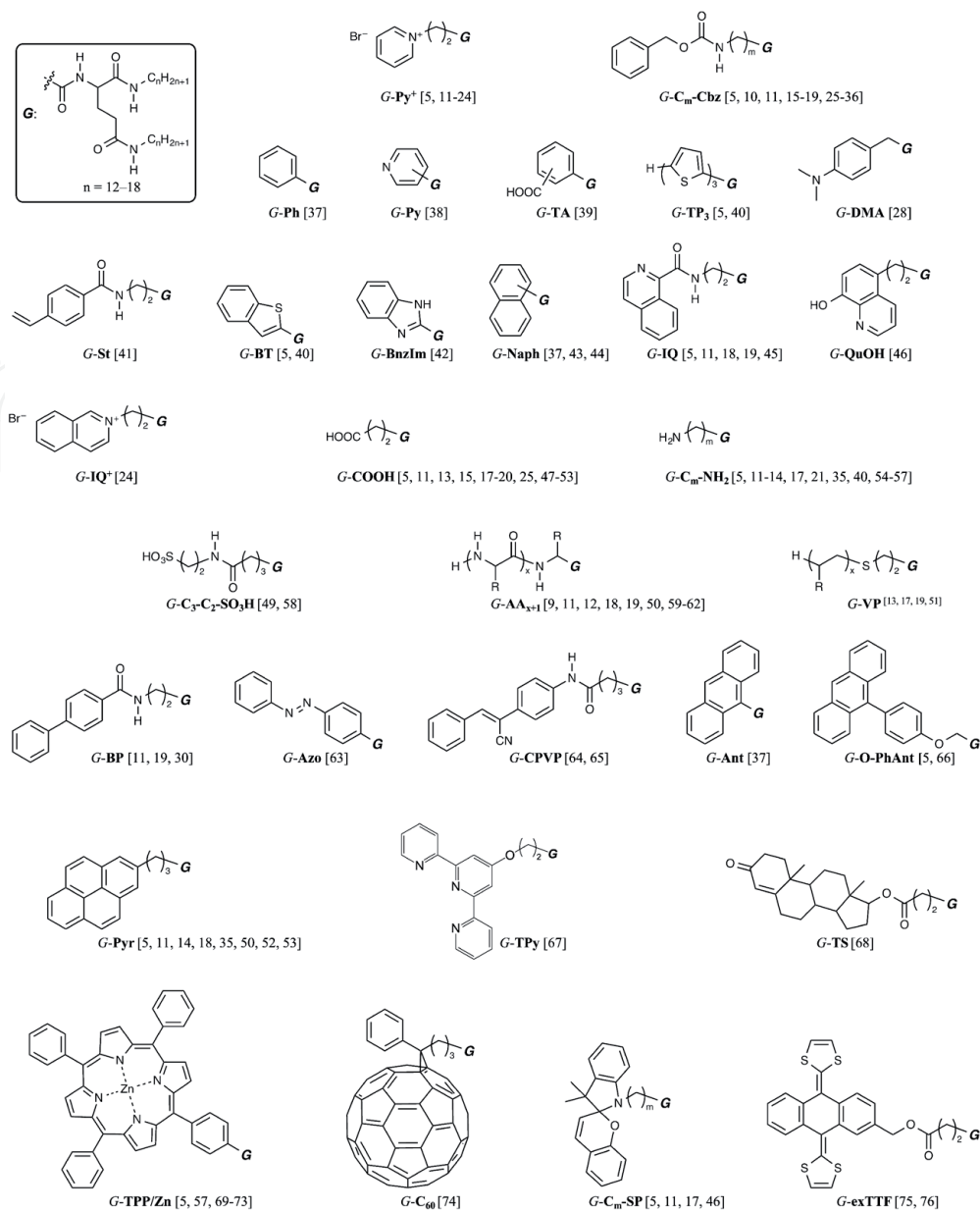
intermolecular interactions and orientation states that are attributed to the molecular design. It is also known that the presence of chirality in the molecular structure tends to make the association form a nanofiber-like structure. After a certain concentration, nanofibers become entangled, resulting in gelation of the solution, which is called a molecular gel or supramolecular gel and is different from a typical polymer gel.

**Figure 3** summarizes amino acid-derived molecular gel-forming materials [5, 9–76] discussed in this chapter.

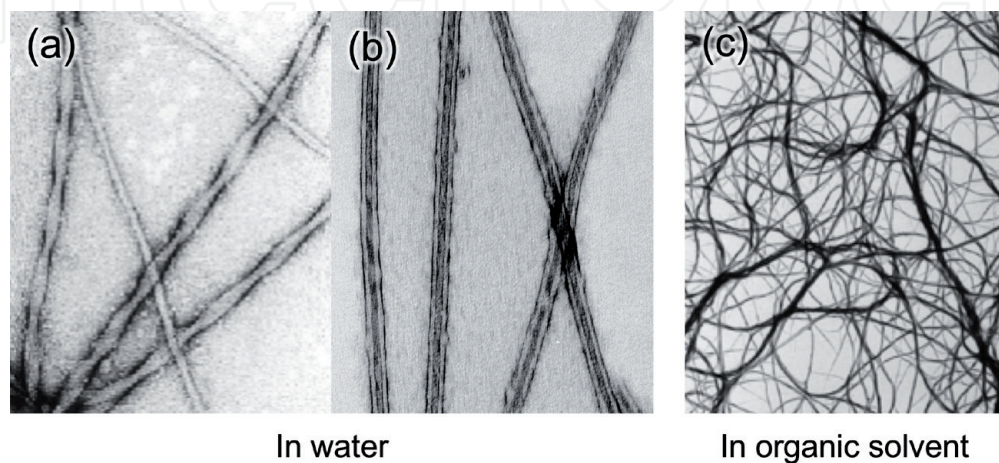
## 2.1 Principle of opt functionalization by molecular gelation

Following are some essential requirements for small molecules to assemble in solution to form nanofibers. (1) The molecule has a part that is dispersible in a solvent, (2) a part that exhibits a relatively strong interaction among molecules, (3) a rigid and non-bulky structure that promotes intermolecular stacking, which is useful as an auxiliary function, and finally, (4) a mechanism that facilitates one-dimensional growth of the association structure set in the molecular structure. The existence of molecular chirality that promotes twisted molecular stacking can be considered the most effective mechanism. A molecular gel comprising a cholesterol derivative, reported by Weiss et al. in 1987, is one of the small molecules that is suitable for this application (**Figure 2**) [7]. However, it has been reported that nanofiber-like aggregates are formed by various low-molecular-weight substances when not limited to the apparent gel state. For example, the authors found that nanofiber-like aggregates could be formed by fibrous bilayer membrane structures in aqueous systems [9, 77]. Since Weiss's report, non-cholesterol derivatives, such as derivatives from amino acid, peptide and polysaccharide, are known as molecular gel-forming substances, and they have led to remarkable developments in this field [78–80].

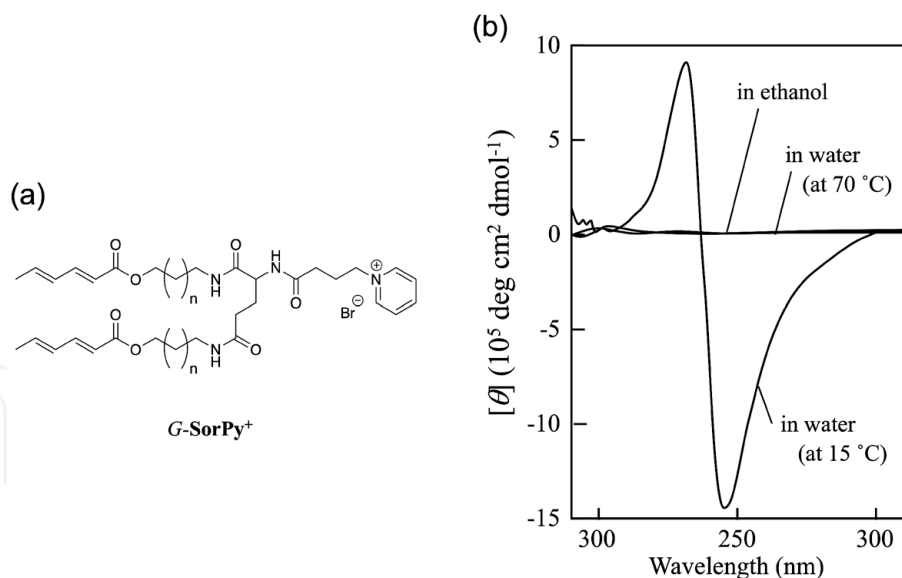
**Figure 3** shows typical amino acid derivatives that produce molecular gels. These molecules satisfy all four requirements described above. These derivatives are more advantageous than cholesteryl derivatives because hydrogen bonds are based on intermolecular interactions, and therefore, by properly tuning the molecular structure, nanofiber structures can be formed in a wide range of solvents, such as water and organic solvents. Further, as shown in the electron micrograph of **Figure 4**, they all form nanofibrillar aggregates although the detailed aggregation morphology differs based on the structure. The formed aggregates have a nano-sized diameter and are rarely bundled, even if they are mixed in the polymer as described later; therefore, there are few whitening due to light scattering. This is an extremely important property for producing a transparent opt functional film.



**Figure 3.** Examples of amino acid-derived molecular gel-forming materials for nanofibrillar network formation [5, 9–76].



**Figure 4.** Typical examples of nanofibrillar aggregates from amino acid derivatives: (a) and (b) were observed by *G-Py*<sup>+</sup> in aqueous systems, and (c) was observed by *G-Cbz* in benzene [12, 25, 81, 82].



**Figure 5.** Chemical structure (a) and CD spectra (b) of *G-SorPy*<sup>+</sup> [12] *G-SorPy*<sup>+</sup> is in a highly ordered state at 15 °C in water.

Molecular gels made from amino acid derivatives often exhibit amplified chirality. Amino acids have an asymmetric center, because of which they act as chiral materials by themselves, and a quite low circular dichroism (CD) intensity, which is a measure of the magnitude of chirality. When these amino acid derivatives are aggregated with hydrogen bonds and a twist in a certain direction occurs in the orientation state, a very large CD signal (Cotton effect) can be obtained; a typical example is shown in **Figure 5**. *G-SorPy*<sup>+</sup> has no asymmetric carbon or optical activity in the sorbyl group. Therefore, the CD signal is not observed in the molecularly dispersed state. On the other hand, when the molecules form an ordered orientation state, a chiral stacking state is created in the sorbyl group (**Figure 5b**), because of which, a very large CD signal is observed around the absorption band of the sorbyl group. Such amplified chirality is often referred to as secondary chirality to distinguish it from chiral-source chirality. That is, the nanofibers produced by self-assembly are likely to exhibit amplified secondary chirality, and this supramolecular function is directly linked to the principle of chiroptical functionalization for polymers, which we will focus on in this section.

## 2.2 Luminous nanofiber

There are roughly two methods for imparting optical functions to self-assembled nanofibers. One is the single-component system, which is a method for introducing a luminescent functional group during molecular design. The other method is the binary system, which is a method for combining self-assembled nanofibers as a template with a luminophore as a guest molecule by molecular interactions such as electrostatic interaction.

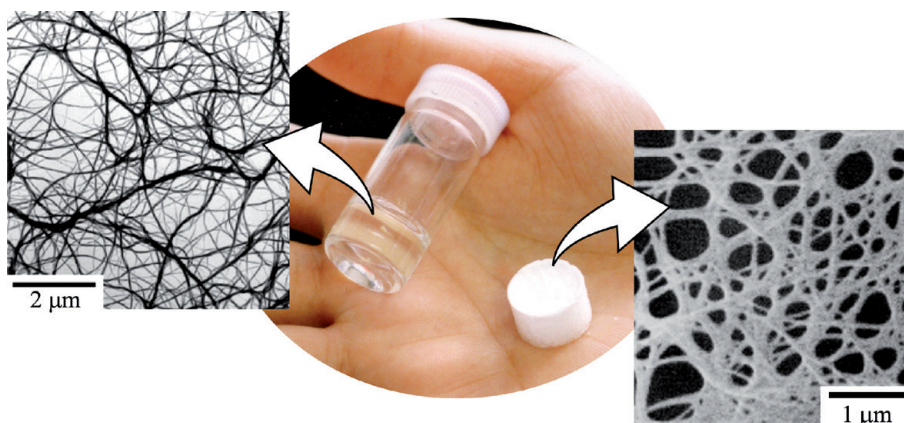
### 2.2.1 Single-component system for chirality enhancement

First, a molecular gel system introduced using pyrene, which is widely known as an organic fluorescent dye, is described. *G-Pyr* in **Figure 3** is an amino acid derivative in which pyrene is introduced. Since *G-Pyr* is a hydrophobic compound, it is insoluble in water but soluble in various organic solvents. When *G-Pyr* is dissolved in hot cyclohexane or toluene to a concentration of approximately 5 mM and

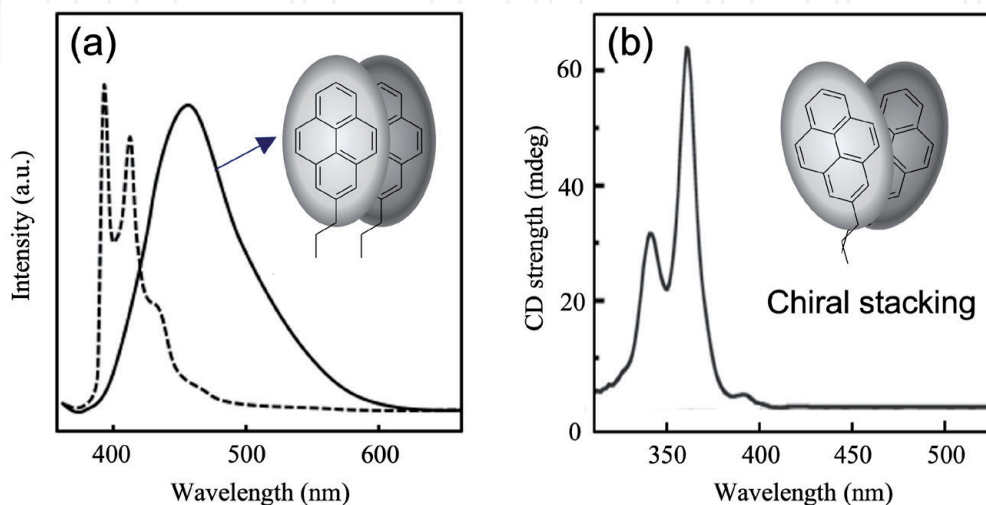
returned to room temperature, it forms a transparent gel [25, 26]. **Figure 6** shows a transparent gel state and a xerogel prepared by freeze drying. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) indicated that clear gel and white solid were formed from fibrous components. When benzene was added to 5 mM *G-Pyr* gel to dilute it to a 0.2 mM mixture, which was heated to form a solution, no gelation was observed even when it was cooled to room temperature. However, the formation of fibrous aggregates was confirmed by TEM observation. These facts conclude that *G-Pyr* forms nanofibers, even under low concentration conditions (apparently in a solution state), that do not form a physical gel state.

When a 0.2 mM benzene solution of *G-Pyr* was excited at 350 nm, corresponding to the absorption maximum of a pyrene group, a fluorescent spectrum with an emission maximum at 455 nm could be obtained, as shown by the solid line in **Figure 7a**. This is characteristic of the excimer from pyrene. No similar spectrum is observed for the starting material, pyrenebutanoic acid (dotted lines in **Figure 7a**), which can be attributed to the monomeric state. These facts suggest that under the condition that *G-Pyr* forms nanofibrillar aggregates, the pyrenyl groups are concentrated from each other, wherein excimers are likely to be formed [26–28].

The CD spectrum also shows the formation of an oriented state by the aggregation of *G-Pyr*. As shown in **Figure 7b**, *G-Pyr* produced from the L-enantiomer produces an extremely large positive signal (Cotton effect). Because there is no chirality in the



**Figure 6.** Benzene gel and xerogel produced by *G-Pyr* and their network structures observed by TEM and SEM [25].



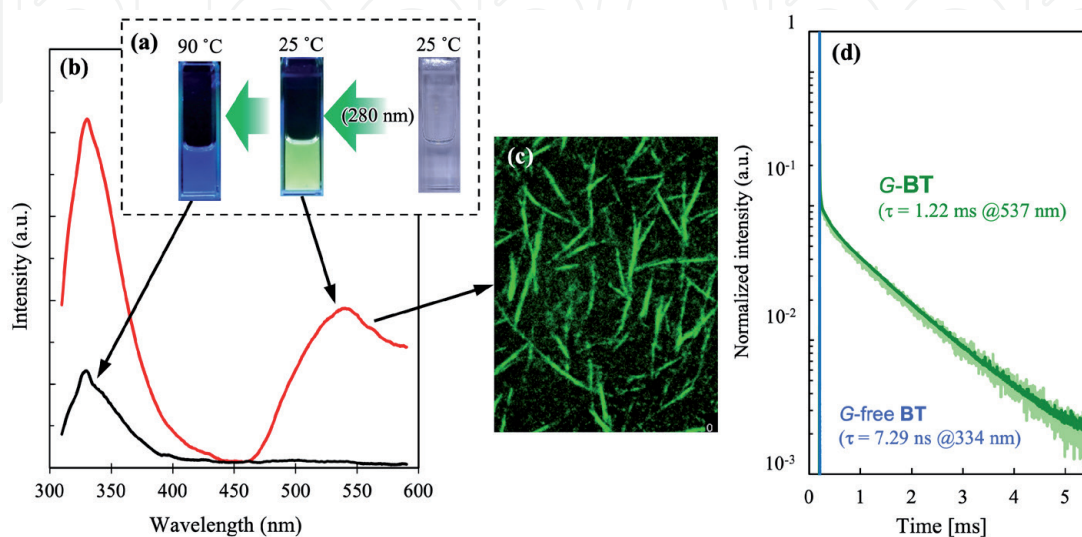
**Figure 7.** Fluorescent (a) and CD (b) spectra of *G-Pyr* solution (0.2 mM in benzene). The dashed line (a) indicates the fluorescent spectrum from pyrenebutanoic acid [26].

pyrene group itself, this suggests chirality induction from an amino acid moiety to the pyrene group. No similar Cotton effect is observed under conditions where *G*-Pyr is in a molecularly dispersed state. To explain this large Cotton effect, it is necessary to consider a phenomenon in which nanofiber-like aggregates are formed by chiral stacking with pyrene groups, as shown in the inset of **Figure 7b**. In *G*-Pyr, three amide bonds around the chiral carbon should be focused on as the driving force for producing a chiral stacking state because when the amide bond is changed to an ester bond, a spherical aggregate morphology called a vesicle is preferentially formed over the nanofibrillar aggregates [26].

*G*-BT is an amino acid derivative with a benzothiophene group as a photofunctional group [82]. When *G*-BT was dissolved in methylcyclohexane, the fluorescent color changed significantly from yellowish green to bluish purple, depending on the temperature (**Figure 8a**). The confocal laser photomicrograph in **Figure 8c** shows that *G*-BT is dispersed in the solution as a fluorescent fibrillar aggregate. Moreover, when observing the fluorescent spectrum, an emission maximum can be observed around 550 nm at room temperature (**Figure 8b**). Since the emission wavelength of the monomer is approximately 330 nm, the Stokes shift differs by nearly 220 nm. This difference is accompanied by that in the fluorescence lifetimes. In fact, it was found that the lifetime in this new emission band around 550 nm was on the order of milliseconds (**Figure 8d**). Presumably, the nanofibrillar aggregates form a stacking state close to the nanocrystals around the benzothiophene group. When heating is used to promote relaxation of this orientation state or trifluoroacetic acid is added as a hydrogen bond inhibitor, the emission around 550 nm disappears and shifts to 330 nm, and the fluorescence lifetime is of the order of nanoseconds, which corresponds to that of the monomeric state of the benzothiophene group.

### 2.2.2 Binary system for chirality enhancement

While the method of obtaining chirality enhancement by the single-molecule system outlined in Section 2.2.1 has a high degree of freedom in molecular design, there are practical limits in the synthetic process. As a solution to this problem, a binary system has been proposed in which a chiral molecular gel is used as a template material with a highly-ordered microenvironment and is combined with a non-chiral luminescent material. The advantage of this approach is that even a



**Figure 8.** Photographs (a), fluorescent spectra (b), confocal image (c), and decay curves (d) of *G*-BT in methylcyclohexane. [83] - reproduced by permission of the Royal Society of Chemistry.



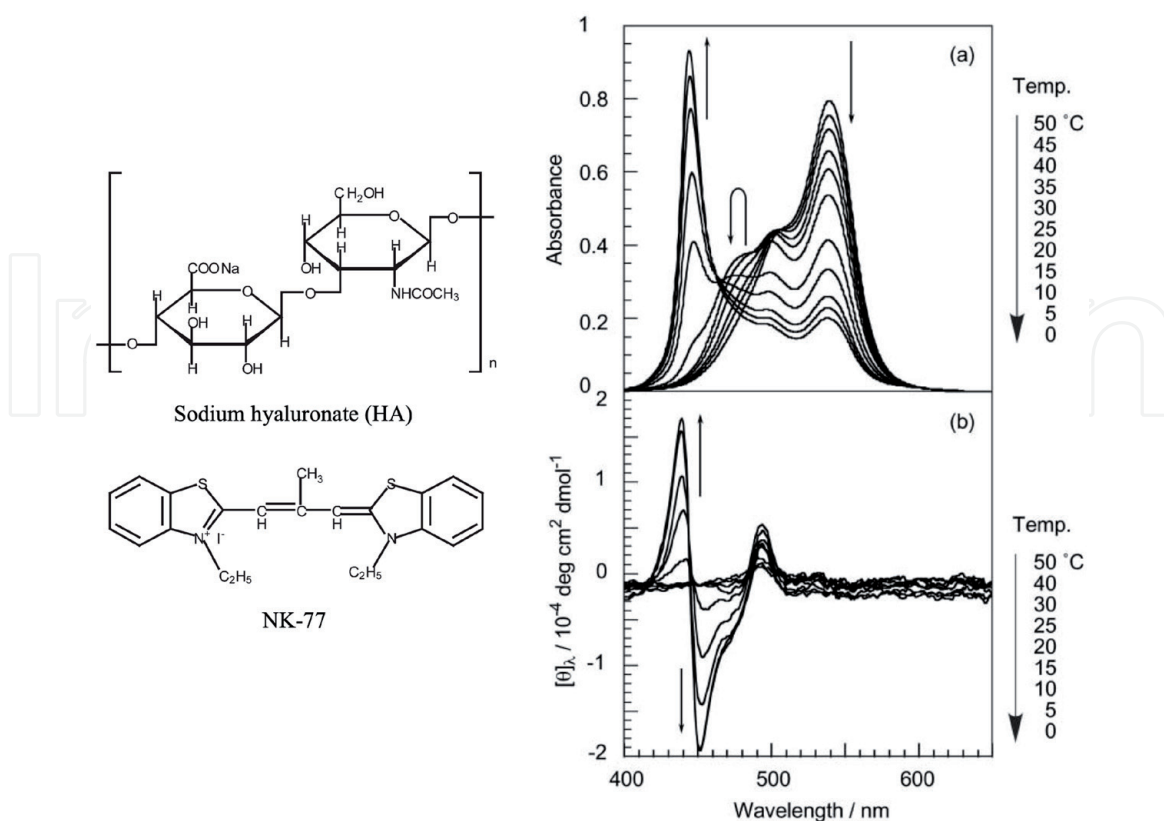
luminescent dye with a complicated structure has few synthetic chemical restrictions because introducing chirality into it is not necessary.

In this method, the wavelength of the amplified CD signals can be easily controlled based on the dye selected by incorporating an appropriate interaction system between the chiral template orientation and the luminescent dye. This idea has been attempted by several researchers over the years. For example, when a polyamino acid with an ionic functional group in the side chain interacts with a particular dye, dimer formation and the accompanying formation of secondary chirality of the dye are observed [84]. A similar phenomenon is observed in the interaction with polysaccharides that form secondary structures [85]. **Figure 9** shows the CD spectra of hyaluronic acid and cyanine dyes. Because there is no asymmetric carbon in the cyanine dye used, it can be concluded that the CD spectra in **Figure 9** are induced.

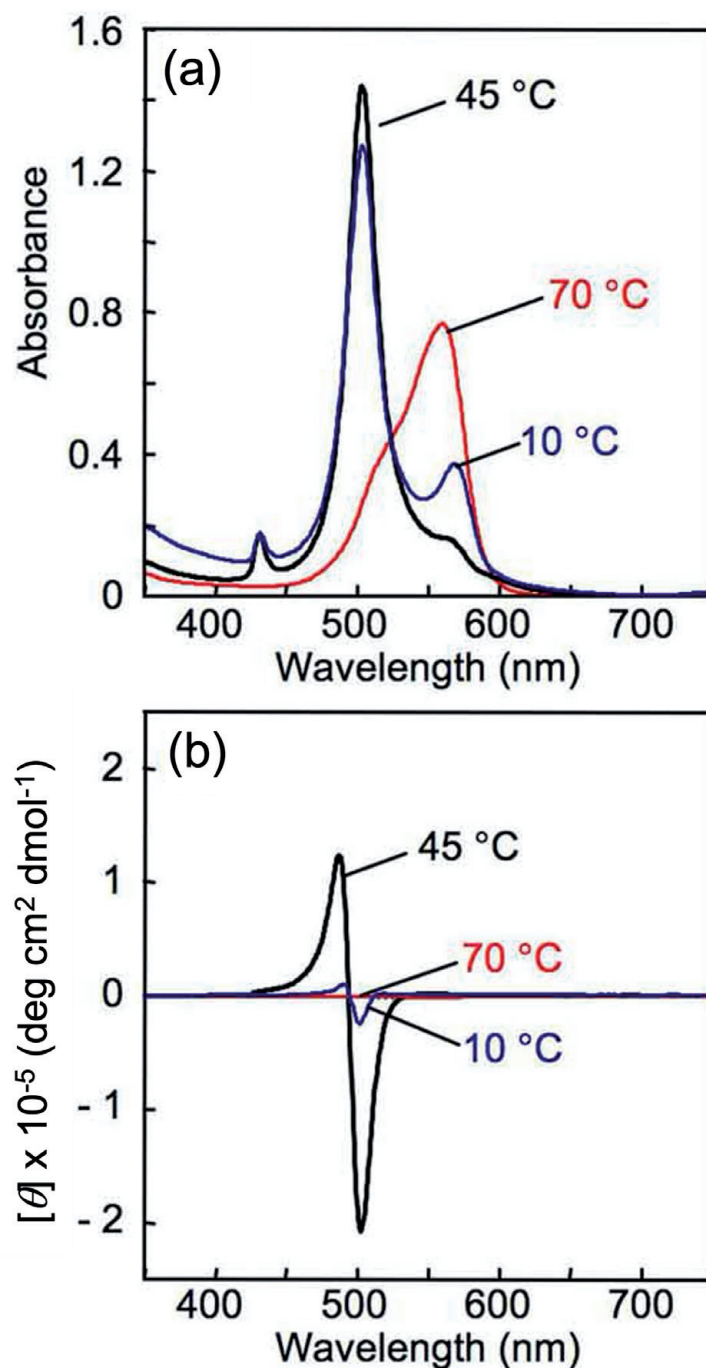
There are many examples of chirality induction due to the combination of molecular gels and non-chiral dyes. **Figure 10** shows an example of induced chirality as the binary system. In this case,  $G\text{-Py}^+$ , which has a pyridinium-based cationic group that promotes electrostatic interaction, is adopted as an amino acid-based molecular gel-forming substance, and it is combined with a selected anionic cyanine-based dye [21]. It was clarified that such induced chirality can be observed even for a single atom such as bromine. **Figure 11** shows an example in which induced chirality is expressed by the binding of bromine ions to a chiral molecular gel generated from a gemini surfactant [86].

### 2.2.3 Stimuli-responsive chirality

Since molecular gelation by a low-molecular-weight compound is a phenomenon induced by molecular assembly, there is a critical gelation concentration, and it



**Figure 9.** Example of induced CD to dye from chiral polysaccharide template. (a) Visible absorption and (b) CD spectra of cyanine dye (NK-77) in the presence of sodium hyaluronate (HA) in MeOH-H<sub>2</sub>O mixture. [85] - reproduced by permission of the Royal Society of Chemistry.

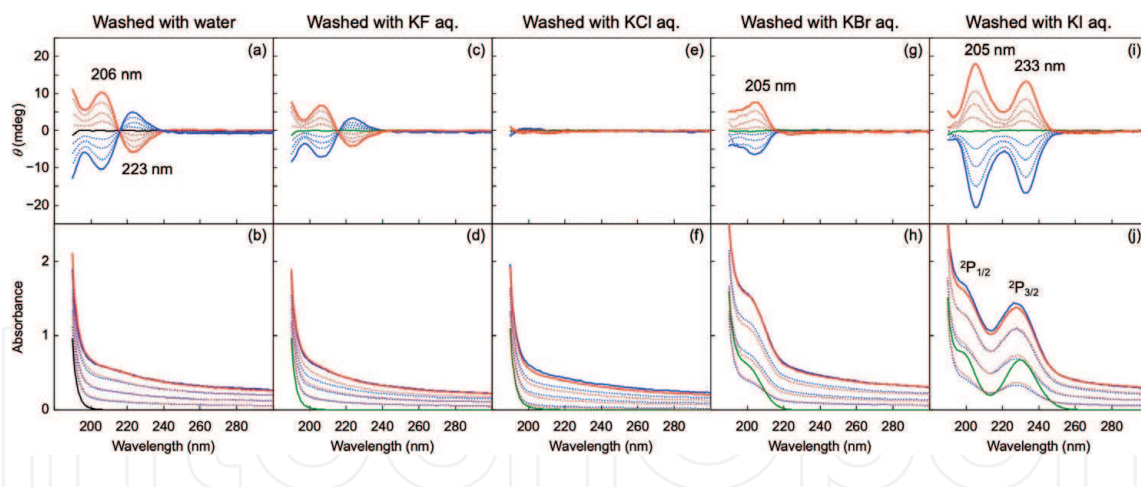


**Figure 10.** Example of induced CD to dye from chiral bilayer membrane template. (a) UV-visible absorption and (b) CD spectra of cyanine dye (NK-2012) in the presence of  $G\text{-Py}^+$  in water. [21] - reproduced by permission of Springer Nature.

varies depending on the kind of solvent. Moreover, the hydrocarbon chain in the molecular structure has a phase transition phenomenon corresponding to the melting point. Therefore, it is easy to understand that molecular gels can have both lyotropic and thermotropic properties.

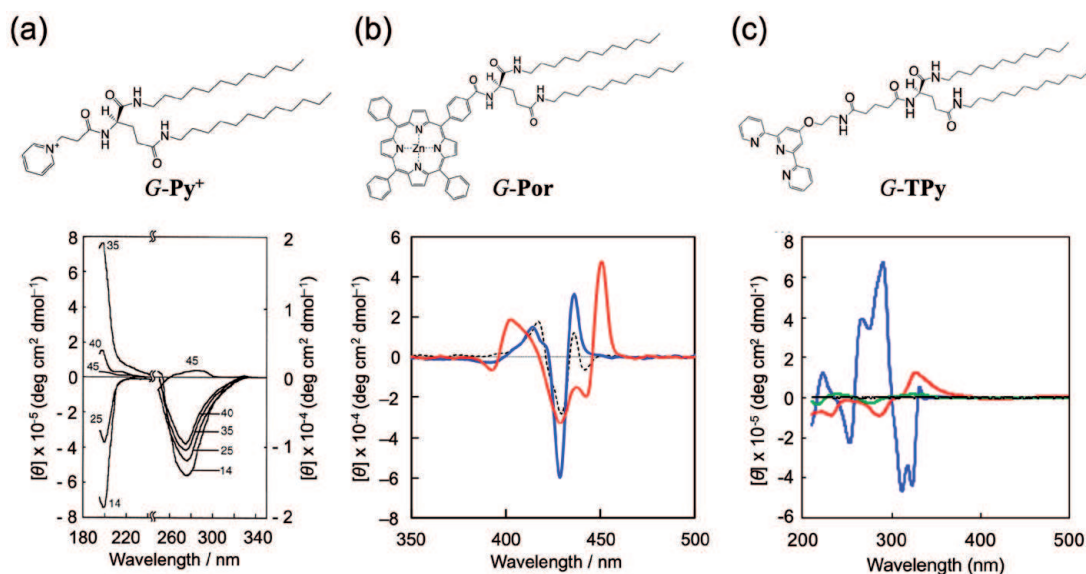
A typical example of a lyotropic property is given in  $G\text{-SorPy}^+$  in **Figure 5**;  $G\text{-SorPy}^+$  exhibits a large CD intensity in water, but not in ethanol [12]. Similar lyotropic behavior can be observed in  $G\text{-Pyr}$ . Its fluorescent color in cyclohexane is remarkably different from that in chloroform, and this is attributed to the difference in their solubilities.

An example of thermotropic behavior is the amino acid derivative  $G\text{-Py}^+$  with a pyridinium group [4, 81]. As shown in **Figure 12a**, the CD intensity varies significantly depending on the temperature. This is because the  $G\text{-Py}^+$  aggregates



**Figure 11.**

Example of induced CD to bromine as a single atom from chiral self-assembly-based template. CD and UV-visible absorption spectra of silica-coated L- (red) and D- (blue lines) self-assembled nanohelices in water ( $0.05\text{--}0.20\text{ mg mL}^{-1}$ ) obtained by washing. Black and green spectra represent water (b) and  $0.05\text{ mM-KX}$  aqueous solutions where X are F (d), Cl (f), Br (h) and I (j). [86] - reproduced by permission of the Royal Society of Chemistry.



**Figure 12.**

Examples of CD responsibilities in  $G\text{-Py}^+$  (a), [4, 81]  $G\text{-por}$  (b), [87] and  $G\text{-TPy}$  (c) [67] assemblies by external factors. [4, 81, 87] - reproduced by permission of the chemical Society of Japan (CSJ). [67] - reproduced by permission of the Royal Society of Chemistry.

have two phase transition temperatures. Beyond these two-phase transition temperatures, the lateral diffusion rate of the molecule increases even in the aggregated state, and the secondary chirality based on the molecular orientation disappears.

Molecular gels are sensitive not only to solvent types and temperatures but also to other external factors. **Figure 12b** shows the CD spectra of the amino acid derivative  $G\text{-Por}$  with a porphyrin as a functional group. In cyclohexane, a very large CD intensity is observed near the absorption band of porphyrin, but since there is no asymmetric carbon or chirality at the porphyrin site, the expression of the large CD signal is attributed to chiral orientation among the porphyrin moieties in cyclohexane gel. The addition of an imidazole derivative to this  $G\text{-Por}$  gel remarkably changes the CD pattern, but such a change does not occur with the addition of pyridine at the same concentration, [87] which is attributed to the different coordination abilities of the guest molecules.

**Figure 12c** shows the CD pattern of a molecular gel with amino acids having a terpyridyl group, *G*-TPy. The intensity and pattern of the CD spectra change significantly depending on the type of metal coordinated to the terpyridyl group [67].

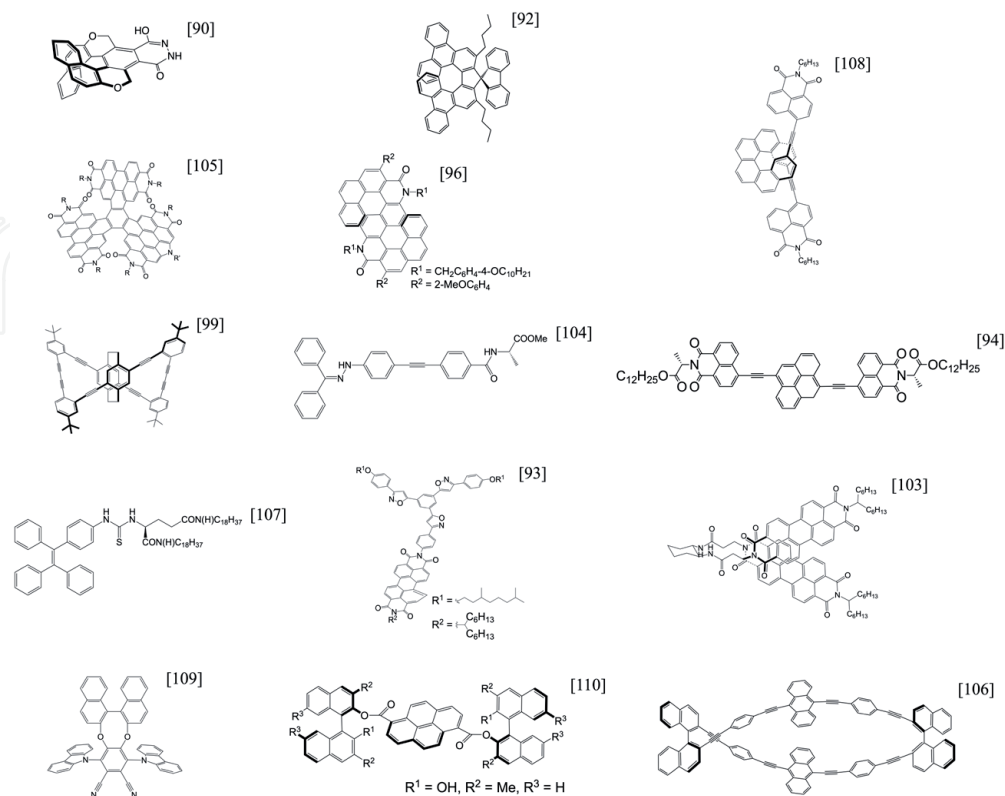
As described above, chiral molecular gels can significantly change chirality with respect to various external factors, so their use for sensing using this responsiveness is also attractive.

### 2.3 Circularly polarized luminescent molecular gel

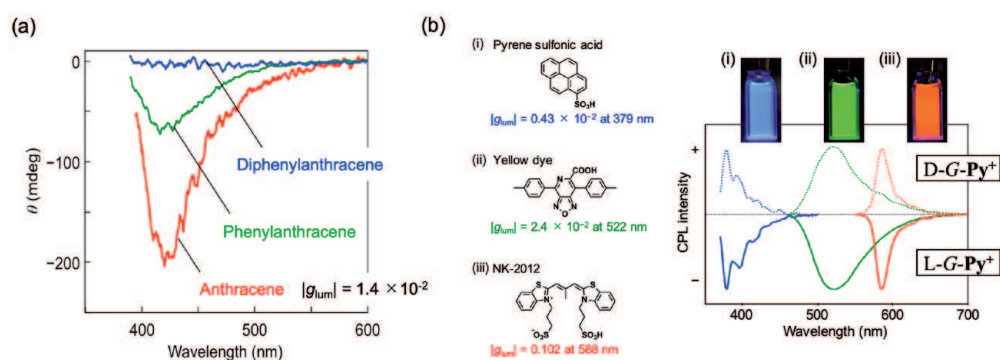
Circularly polarized luminescence (CPL) is angle-independent and contains light information not found in normal light, and therefore, it is expected to be used in various applications. Potential applicability is found in many industrial fields such as biometric recognition systems, light sources for plant factories, storage memories, and 3D displays. On the other hand, considering organic materials that generate CPL, although there are numerous research results, [88–110] their strength (optical purity) is low and they have not yet been put into practical use.

**Figure 13** summarizes the structural formula of single-molecule CPL-generating dyes [90, 92, 94, 96, 99, 103–110]. Most conventional organic materials that generate CPL are chiral fluorescent dyes that utilize the twisting and straining of molecules, [90] and therefore, require complicated chemical synthesis and purification processes. To overcome these problems and fabricate a CPL generation system with higher optical purity, the authors utilized self-assembled nanofiber systems formed from amino acid-derived molecular gels.

As mentioned in Section 2.1, *G*-Pyr is a fluorescent substance with chirality; therefore, it is considered as a good candidate, but the resultant CPL intensity ( $g_{\text{lum}}$  value) was of the order  $10^{-3}$  [66]. It is not superior to the chiral organic fluorescent molecules reported so far. One reason for this has emerged as an inference that there is no optical activity in the excimer emission of pyrene.



**Figure 13.**  
Examples of CPL-generating fluorescent dyes [90, 92, 94, 96, 99, 103–110].

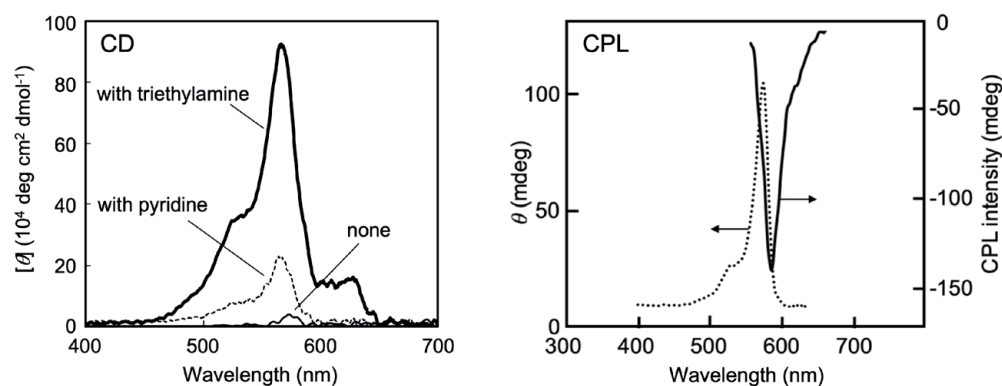


**Figure 14.**

Example of induced CPL by a binary system constructed of non-chiral fluorescent dye with chiral molecular gel template. (a) CPL spectra of anthracene, phenylanthracene, and diphenylanthracene in the presence of  $G\text{-Py}^+$  in aqueous solutions at 2 °C. Excitation wavelength was 340 nm. [Anthracene derivatives] = 12.5  $\mu\text{M}$ . [ $G\text{-Py}^+$ ] = 0.5 mM. [81] - reproduced by permission of the Chemical Society of Japan (CSJ). (b) Tunability of CPL emission bands. Blue, green, and red CPL spectra were obtained with (i) pyrenesulfonic acid, (ii) Yellow dye, and (iii) NK-2012, respectively. All the CPL spectra were measured in aqueous systems at 20 °C in the presence of L- and D-enantiomers of  $G\text{-Py}^+$  with fluorophores. The concentrations of  $G\text{-Py}^+$  and the fluorophores were 0.5 mM and 12.5  $\mu\text{M}$ , respectively. The excitation wavelengths were 330, 420, and 500 nm in pyrenesulfonic acid, Yellow dye, and NK-2012. All the CPL spectra were normalized at the highest peak of the fluorescence emissions corresponding to the CPL signals. [24] - reproduced by permission of John Wiley and Sons.

On the basis of this finding, we applied a binary method wherein an existing non-chiral fluorescent dye was incorporated into a molecular gel as a chiral template for CPL generation. This method is advantageous because it is not necessary to introduce chirality into the fluorescent dye, because of which, the degree of freedom in synthetic chemistry is greatly increased. In addition, the light emitting region of the CPL can be easily tuned by proper selection of the dye. As a result, the highest value in CPL ( $|g_{\text{lum}}| > 0.1$ ) was obtained using a molecular gel from  $G\text{-Py}^+$  as a chiral template with a hydrophobic fluorescent dye such as anthracene (Figure 14a) [81] and an anionic cyanine-based fluorescent dye (Figure 14b) [24] combined. Figure 14b also shows that the emission wavelength can be easily tuned by selecting pyrene sulfonic acid or yellow dye as the fluorescent dye and that the positive and negative can be reversed by the enantiomers of the template [24].

The other example of CPL generation is presented by Figure 15 [111]. In this case, the  $G\text{-COOH}$ -based molecular gel having a carboxyl group is used as a chiral template, considering solubility in a non-aqueous solvent. It was confirmed that the induced CD and the induced CPL were expressed in the binary system combined with the cationic dye. However, in this case, it was also confirmed that the coexistence of a base such as triethylamine in the solution significantly improved



**Figure 15.**

Induction of CD and CPL in non-aqueous molecular gel system. [111] - reproduced by permission of the Royal Society of Chemistry.

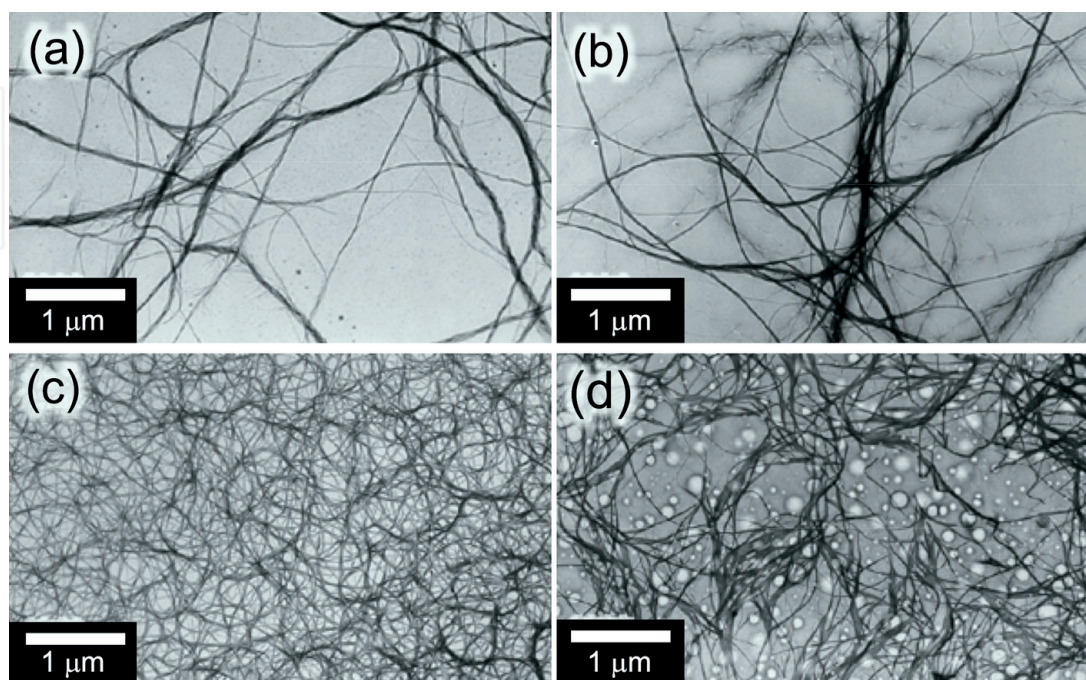
its strength. Probably because of the insufficient acidity of the carboxyl group, neutralization of the anions in the cationic dye promoted a strong interaction between the dye and the chiral template.

### 3. Application for chiroptical polymer film

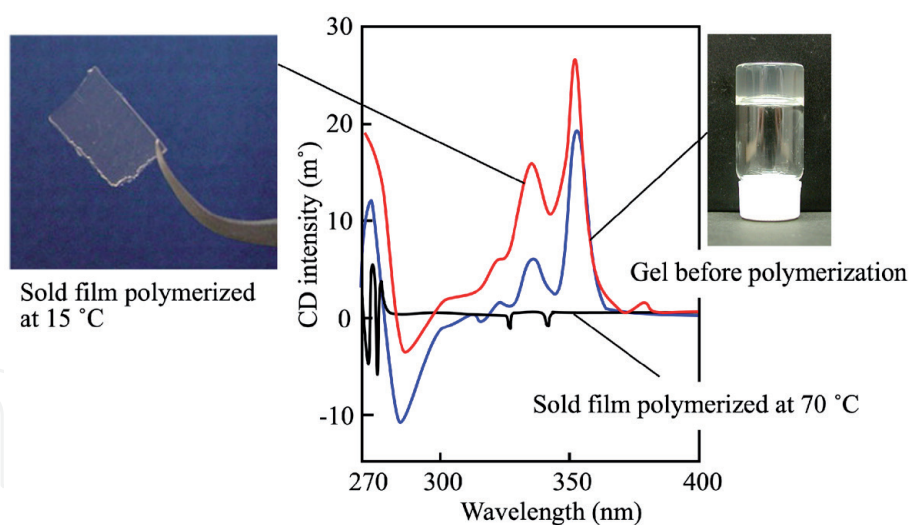
#### 3.1 Encapsulation of chiral nanofiber into polymer

*G-Pyr* forms nanofibers in various polymerizable monomers, such as styrene, divinylbenzene, methylmethacrylate, and methylacrylate (**Figure 16**) [27]. For example, when *G-Pyr* is dissolved in methyl methacrylate at a concentration of 1 wt% and photopolymerized in a sandwich cell in the presence of a suitable photosensitizer, a transparent solid film can be obtained (**Figure 17**). When observing the CD spectrum of the obtained solid thin film, a CD signal showing a chiral orientation of pyrene groups was observed (**Figure 17**, red line). Since the strength and pattern are similar to those before polymerization (**Figure 17**, blue line), it is clear that the chiral orientation state of *G-Pyr* is fixed in the solid thin film. On the other hand, when photopolymerization was performed at 70 °C, a colorless and transparent solid thin film was also obtained, but almost no CD signal was detected (**Figure 17**, black line). That is, it is shown that the molecular orientation state cannot be obtained even if polymerization is carried out under the condition that the molecular orientation is not formed (nanofibers are not formed at 70 °C).

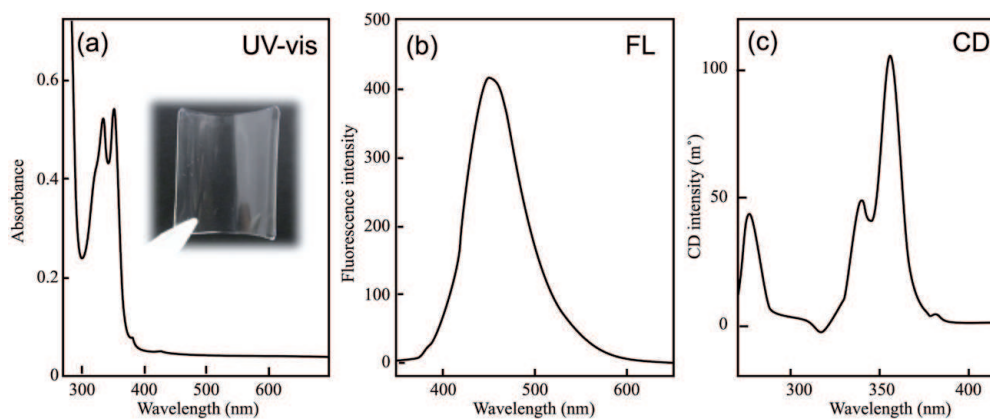
A more convenient method for producing a nanofiber composite polymer film is casting method that uses a polymer solution of general-purpose polymers such as polystyrene (PSt), polymethylmethacrylate (PMMA), and poly (ethylene-vinyl acetate) copolymers (EVA) [24, 82, 112–114]. **Figure 18** shows the CD and fluorescent spectra of a cast film prepared by spin coating from a PSt solution containing *G-Pyr*. **Figure 18** clearly shows that the excimer state (b) and the chiral stacking state (c) observed in the solution are reproduced in the polymer thin film [115].



**Figure 16.** Aggregation morphology of *G-Pyr* in various polymerizable monomers: [27] (a) styrene; (b) divinylbenzene; (c) methylmethacrylate; and (d) methyl acrylate.



**Figure 17.** CD spectra of *G-Pyr* in methylmethacrylate before and after polymerization [27].



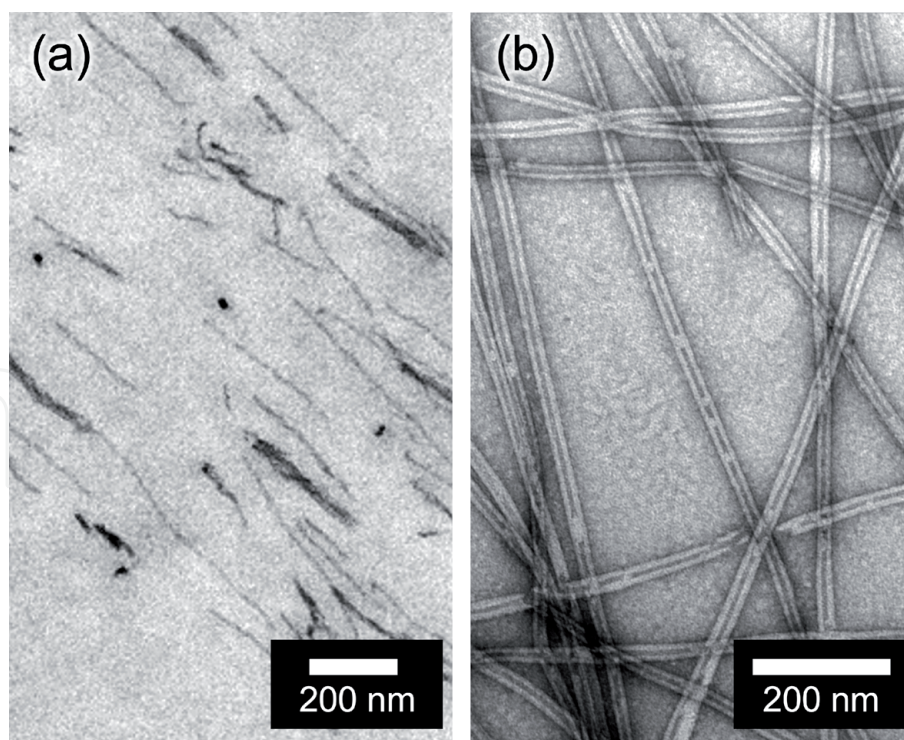
**Figure 18.** UV-visible (a), fluorescent (b) and CD (c) spectra of *G-Pyr*-containing polystyrene film prepared by casting from polymer solution. [115] - reproduced by permission of John Wiley and Sons.

The formation of nanofibers derived from the molecular gelation phenomenon in the polymer can also be detected by direct observation with an electron microscope [112]. As shown in **Figure 19a**, when an EVA film containing *G-Pyr* is stained with an osmium plasma coater, it can be confirmed that nanofiber-like aggregates with a diameter of 10 nm or less are formed in the EVA film. On the other hand, for highly polar polymers, amphipathic *G-Py*<sup>+</sup> can be composited, and hollow nanofibers (**Figure 19b**) are formed in the polymer.

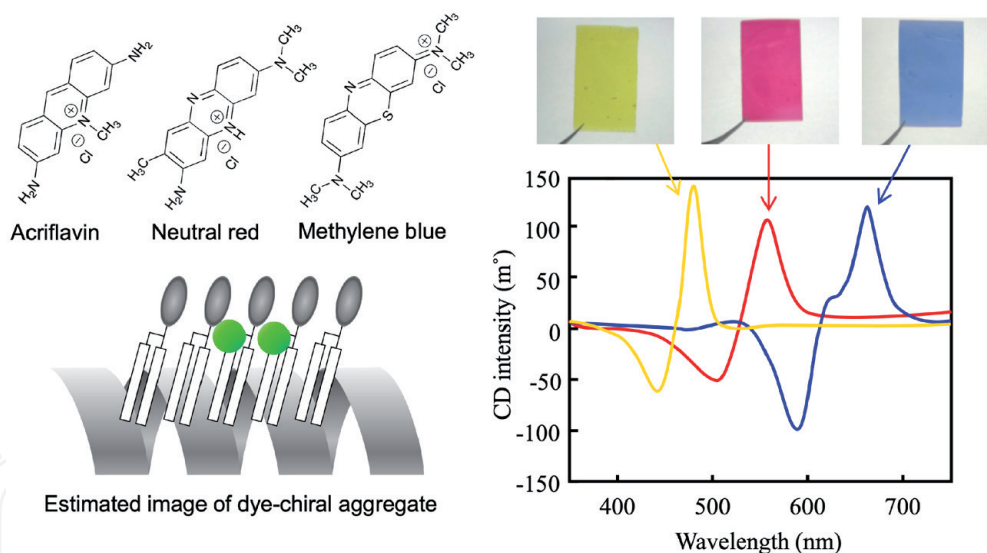
In the casting method, it is also possible to entrust the optical function to the added dye. **Figure 20** shows an example when an anionic molecular gel with *G-COOH* is used as the chiral nanofiber source. After preparing a transparent cast film consisting of a dye-nanofiber-polymer system to which three kinds of cationic dyes were added, distinct CD signals were detected around each absorption band of the added dyes (**Figure 20**). Because the dye does not have any chiral carbon or chirality by itself, the obtained CD signals cause the added dye to electrostatically bind to the chiral nanofibers in the polymer film. Therefore, they are induced CD [50].

### 3.2 Organic room temperature phosphorescent film

A transparent film, as shown in **Figure 21**, can be produced by preparing a mixed solution containing *G-BT* and EVA and forming a film by the casting



**Figure 19.** TEM images of (a) *G-Pyr* aggregates in poly(ethylene-vinylacetate) [112] and (b) *G-Pyr*<sup>+</sup> in polyvinylpyrrolidone [5]. Stained with (a) osmium and (b) uranyl acetate.



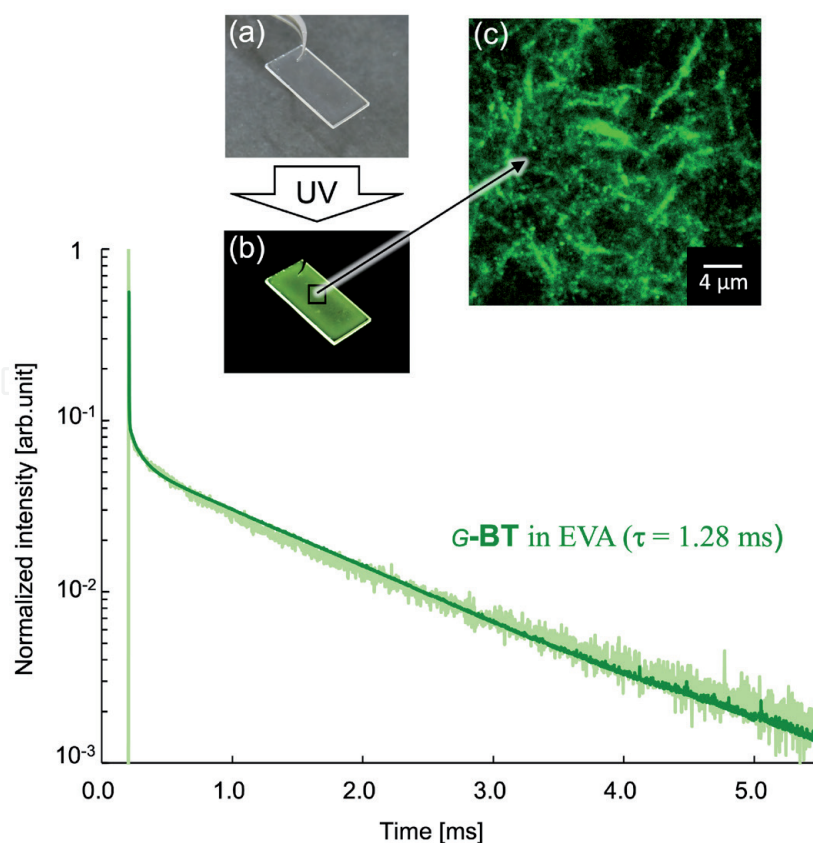
**Figure 20.** Tuning of induced CD in dye-polymer mixed films [50].

method. The obtained film maintains a high Stokes shift and millisecond-order fluorescence lifetimes, likely to that of the solution systems. That is, the orientation state in the solution is also formed in the polymer. The formation of nanofibers in the polymer can be confirmed by laser microscopy in **Figure 21c** [83].

### 3.3 CPL polymer film

**Figure 22a** shows a glass plate in which polystyrene with a composite CPL source is cast on one side. The CPL source is a binary system using a molecular gel from *G-COOH* and a cationic cyanine dye [111]. Nanofibrils are detected using confocal microscopy in the polymer film, as shown in **Figure 22b**. **Figure 22c** shows





**Figure 21.**

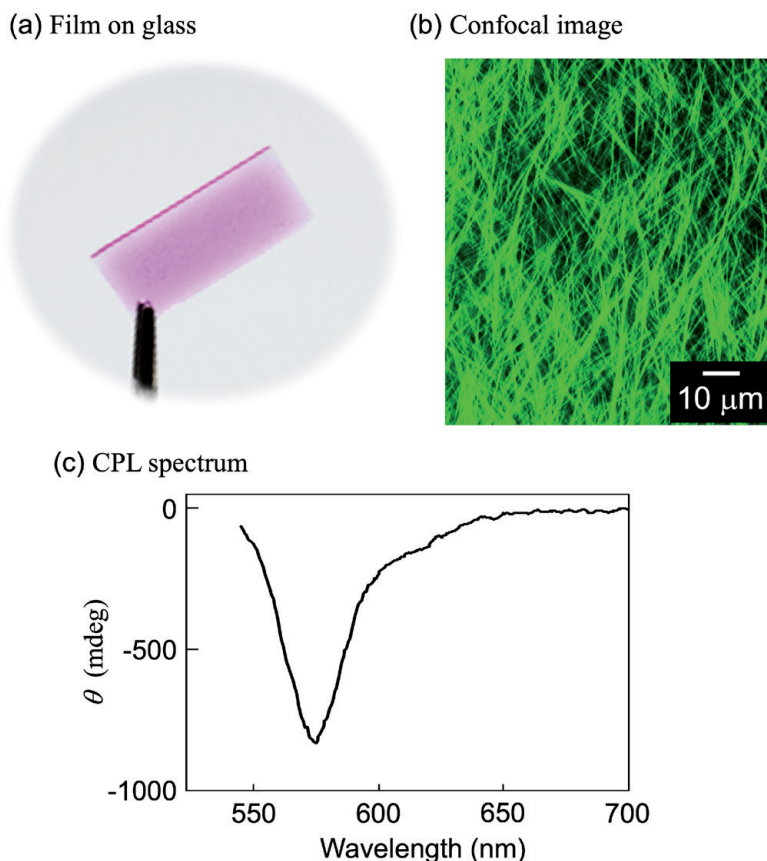
Example of room temperature phosphorescence by G-BT-containing polymer film. Luminescence decay curves were obtained at 525 nm. The photographs (a) and (b) are the G-BT-containing polymer film on quartz glass under normal and UV lights, respectively. (c) Confocal image of the G-BT-containing polymer film was obtained with excitation at 488 nm [83] - reproduced by permission of the Royal Society of Chemistry.

the CPL spectrum of this film, in which the spectral shape and emission wavelength are similar to the results observed in its solution system. These facts indicate that the nanofiber and composite structure of the dye formed in the solution system were maintained as they were in the polymer.

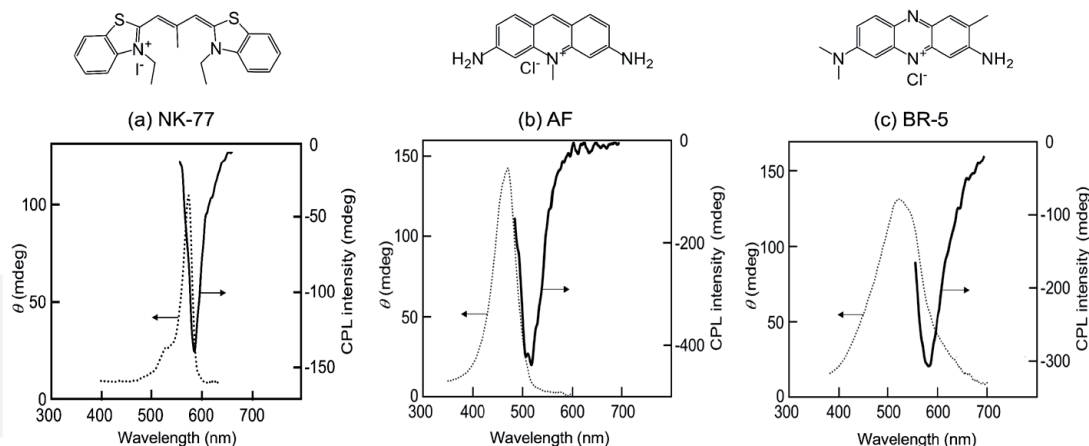
Cyanine-based dyes, such as NK77 and 2012, are attractive as they combine with molecular gels to ensure good CPL strength; however, they are fragile due to light resistance. Therefore, binarization with a more chemically stable fluorescent dye is required. **Figure 23** shows the CPL spectra of a polymer film fabricated in combination with a more light-resistant dye, [111] ensuring good CPL strength and light resistance.

### 3.4 Application for wavelength conversion

The wavelength of sunlight and artificial lights cannot always be suitable for their applications, and light management using methods such as shading, wavelength cutting, and polarization is required depending on the application. In silicon-based solar cells, the spectral sensitivity to ultraviolet and near-infrared lights is low. Therefore, high energy levels of ultraviolet light are cut by glass. In order to effectively utilize unused light, it is necessary to introduce a technology that converts unnecessary ultraviolet and near-infrared light into visible light. Various fluorescent materials that use rare earths are leading the way in this field of application: nitride systems containing europium ions ( $\text{Eu}^{2+}$ ) and cerium ions ( $\text{Ce}^{3+}$ ) as activators, and rare earth materials such as garnet-based materials are used as fluorescent materials for lamps and white LEDs [116]. On the other hand, rare earth-free and low-toxic dyes are also required, and therefore, many organic fluorescent dyes have been



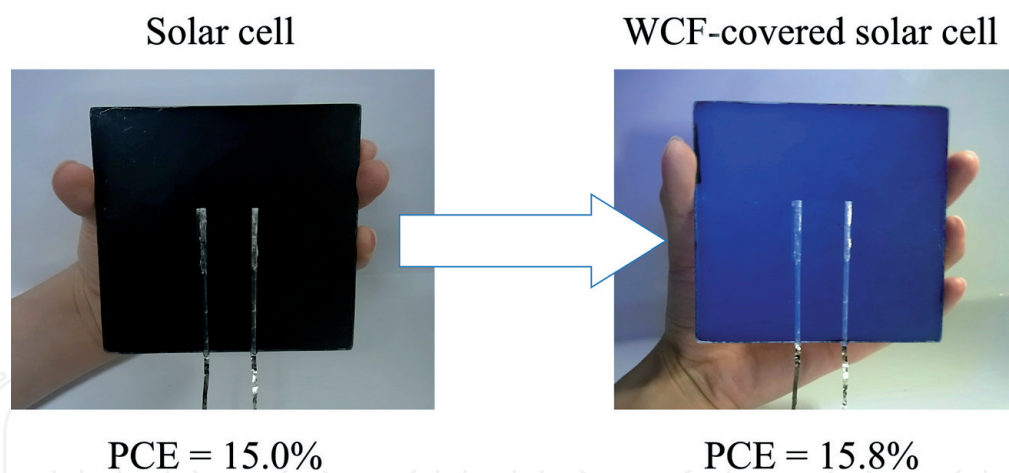
**Figure 22.** Aggregation morphology and CPL spectrum of the polystyrene composite film from the dye (NK-77) with G-COOH system. [111] - reproduced by permission of the Royal Society of Chemistry.



**Figure 23.** Induction of strong CPL from the composite polymer film from various fluorescent dyes with chiral molecular gel system. [111] - reproduced by permission of the Royal Society of Chemistry.

developed [112, 115, 117–119]. Lightness, flexibility, and excellent processability are essential advantages of organic materials.

In this chapter, we will introduce the optical modulation function using self-assembled fluorescent nanofibers. As shown in **Figure 7**, a polymer film in which G-Pyr is embedded in polystyrene absorbing light in the UV-A region, which is not absorbed by ordinary inorganic glass, and it emits visible light. **Figure 24** shows an example in which a polymer system consisting of a G-Pyr-EVA composite is applied to the surface of a CIGS-based solar cell. Comparing the conversion efficiencies using simulated sunlight (AM1.5), it was confirmed that the power generation



**Figure 24.**

*Application of the wavelength conversion film (WCF) for CIGS solar cell. [6] - reproduced by permission of John Wiley and Sons.*

efficiency before coating increased from 15.0% to 15.9% due to coating [112]. This increase in conversion efficiency is attributed to the fluorescent nanofibers embedded in the polymer film that absorb ultraviolet (UV-A region) light with low spectral sensitivity of the solar cell and have an emission peak in the visible region (~460 nm by excimer emission) with high spectral sensitivity.

#### 4. Conclusions

In this chapter, we describe the characteristics of self-assembled nanofibers generated from amino acid-derived molecules, the expression principle of their unique optical properties, and their complexing with polymers. Since self-assembled nanofibers are structures formed by non-covalent bonds, one side that is physically fragile remains. However, conventional problems related to the dispersion of nanofibers are solved, and complicated dispersion techniques and surface modification processes that cause harmful effects are not required. Therefore, it is a material that enables higher-order functionalization of the polymer material while maintaining characteristics of the bulk polymer. In addition, various techniques for complementing vulnerabilities have been proposed. The optical management film with the optical modulation function introduced in this chapter is expected to be used not only for solar cells but also for various applications such as housing, automobiles, displays, artificial lighting, and plant factory lighting. We hope that the methodology using molecular gel-based functionalization can provide findings for further development.

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#### Conflict of interest

The authors declare no conflict of interest.

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### **Author details**

Hirota Iahara<sup>1,2\*</sup>, Makoto Takafuji<sup>2</sup> and Yutaka Kuwahara<sup>2</sup>

1 National Institute of Technology, Okinawa College, Nago, Japan

2 Kumamoto University, Kumamoto, Japan

\*Address all correspondence to: [ihara@kumamoto-u.ac.jp](mailto:ihara@kumamoto-u.ac.jp)

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