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Finely Controlled Circularly Polarized Luminescence of a Mechano-Responsive Supramolecular Polymer

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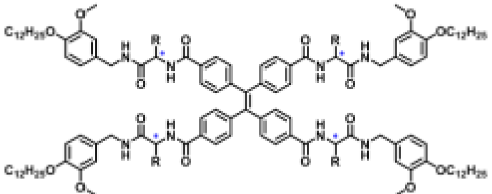
Abstract: We report on finely controlled circularly polarized luminescence (CPL) supramolecular polymerization based on a tetraphenylethene core with four *L*- or *D*-alanine branch side chains (*L*-**1** and *D*-**1**) in the solution state resulting from the tuning of mechanical stimulus. Weak, green emissions of *L*-**1** and *D*-**1** in tetrahydrofuran (THF) were converted to strong blue emissions by tuning the mechanical stimulus. The strong blue emissions were caused by an aggregation-induced emission (AIE) effect during the formation of a supramolecular polymer. Lag time in the supramolecular polymerization was drastically reduced by the mechanical stimulus, which was indicative of the acceleration of the supramolecular polymerization. Interestingly, a significant enhancement of circular dichroism (CD) and CPL signals of the *L*-**1** and *D*-**1** was observed by tuning the rotational speed of the mechanical stimulus, which implies that the chiral supramolecular polymerization was accelerated by the mechanical stimulus. These results imply that the CPL signals were tuned by the strength of the external mechanical stimulus.

Circularly polarized luminescence (CPL) is a unique chiroptical property of chiral emission systems and regarded as one of the most important tools for investigating the excited-state properties of chiral materials.[1-15] Materials exhibiting CPL are of great interest not only for understanding the mystery of chirality but also for potential important applications, such as chiroptical recognition sensors,[8,9] noninvasive biomedical diagnosis in the biological field,[10-13] and catalysts for asymmetric chemical synthesis.[14,15]

Mechano-responsive materials also usually exhibit emission properties under mechanical stress.[16-18] In most cases, this effect results from the formation of supramolecular nanostructures; mechanical stimulus triggers transitions between several crystalline and amorphous phases or between an aggregated and a monomeric state, which are responsible for changes in the luminescence emission.[19-25] Although mechano-responsive materials have been developed for mechanical stress sensing[20] and security tag applications,[21] owing to the limit of expression of both chirality and luminescence properties, mechano-responsive materials that enable control of CPL characteristics have been only two studies reported by Kawai[24] and Yamashita[25] groups. In previous studies, the researchers have reported the control of chirality in hydrogels composed of two components and a luminescence dissymmetry factor of two difluoro-boron-β-diketonate complexes. In contrast, the kinetically controlled mechano-responsive chiral supramolecular polymerization through the control of CPL property has not been reported, despite their benefits as the seed and building block in living supramolecular co-polymerizations. Therefore, the investigation of CPL supramolecular polymerization generated by a finely tuned external stimulus (e.g., rotation, pressure, and light) still remains a significant challenge. Here, we report on kinetic controlled CPL supramolecular polymerization with four *L*- or *D*-alanine branch side chains formed by the fine-tuning of a mechanical stimulus. Interestingly, CD and CPL signals were able to be finely tuned by controlling rotational speed; increasing the rotational speed led to the acceleration of a large enhancement of CD and CPL signals.



L-**1** (*L*-form): R = -CH_3
D-**1** (*D*-form): R = -CH_3
2: R = -H

Our molecules *L*-**1**, *D*-**1** and **2** were designed using a typical strategy utilized in the study of supramolecular polymers based on tetraphenylethene molecule bearing hydrogen-bonding moieties and long alkyl chains. In particular, a tetraphenylethene core of *L*-**1** and *D*-**1** in the supramolecular polymers was introduced due to unique aggregation-induced emission (AIE) characteristics with the external stimulus. *L*-**1** and *D*-**1** were also expected to helically self-assemble through the CH-π stacking of tetraphenylethene planes and the intermolecular hydrogen bonding of amide groups. Compound **2** was prepared as a reference to the essential role of chiral moiety in CPL supramolecular polymerization.

The absorption and luminescence spectra of *L*-**1**, *D*-**1** and **2** were first observed using a constant clockwise rotational speed in tetrahydrofuran (THF). As shown in Figure S1A, the maximal absorption band was located at 333 nm in the THF without stirring. The absorption band slowly shifted to 338 nm for 4.5 h. In contrast,

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interestingly, the maximal absorption band of *L*-**1** at 333 nm in the THF rapidly shifted to 338 nm, within one isosbestic point, by tuning the rotational speed from 200 to 1,000 rpm (Figure S1B). These absorbance changes were dependent on the clockwise rotational speed, and the spectral changes suggested that monomeric molecules of *L*-**1** with twisted conformation were quantitatively converted to the supramolecular polymer by tuning the mechanical stimulus.

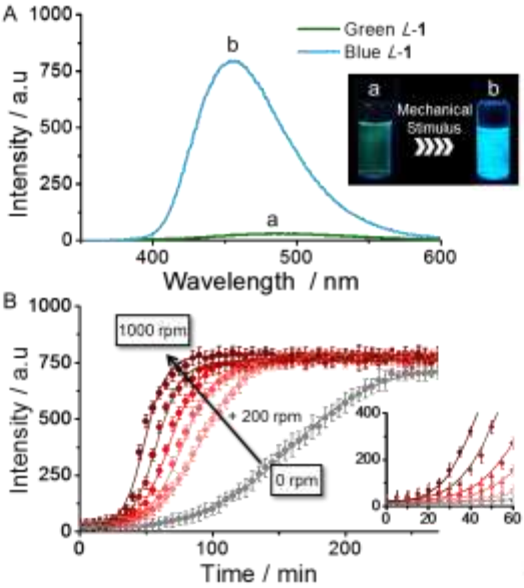
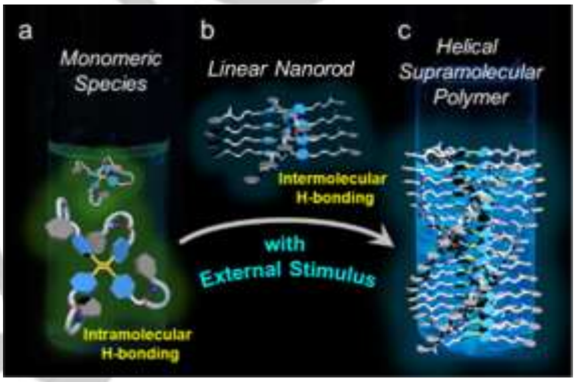


Figure 1. (A) Luminescence spectra of (a) green and (b) blue *L*-**1** (2.5×10^{-5} M) in THF. (B) Plot for luminescence intensity of *L*-**1** obtained by different rotational speeds at 455nm *vs* time.

In addition, a *L*-**1** broad, green and weak emission band was obtained without rotation at 500 nm (λ_{ex} = 333 nm) in the THF (Figure 1A). Interestingly, the luminescence spectrum of *L*-**1** shifted to 455 nm over time, and the emission color changed from green to blue. The luminescence intensity of *L*-**1** at 455 nm was ~500-fold higher than that exhibited by the green emission. This intense enhancement of the luminescence intensity was due to the AIE effect in the formation of the supramolecular polymer. This AIE effect with the blue emission was due to a larger torsion angle and a more twisted conformation and stacking tetraphenylethenes.[26] Therefore, we observed luminescence spectral changes at various clockwise rotation speeds (i.e. 200, 400, 600, 800, and 1,000 rpm) (Figures S2 and 1B). Interestingly, a plot of the luminescence intensity at 455 nm as a function of time shows a typical sigmodal curve characterized by a nucleation-elongation mechanism with lag time when a solution of *L*-**1** was maintained without rotation. This long lag time was due to the presence of an intramolecular hydrogen-bond between the amide groups of the alanine moieties in *L*-**1**, which restricted the rapid growth of the supramolecular polymer.[27] The lag time in the supramolecular polymerization was drastically reduced by increasing the rotation speed, and the luminescence intensity reached a maximum within 90-155 min (Figure 1B). The weak green emission was rapidly converted to a blue emission when the rotation speed was 1,000 rpm. This was attributed to the formation of the supramolecular polymer via the intermolecular hydrogen-bonding interaction by the dissociation of the intramolecular hydrogen-bond formed in the monomer *L*-**1** by the mechanical stimulus. These findings indicate that the external mechanical stimulus accelerated the supramolecular polymerization, which is the first example of supramolecular polymerization promoted with a mechanical stimulus. In addition, we observed a change in the luminescence spectra depending on the sample concentration, stirrer size, and vial size (Figures S3–S5). The increase in luminescence intensity at 455 nm was accelerated depending on the concentration of *L*-**1**. In contrast, the stirrer size with a constant vial diameter and the vial size did not affect the changes in luminescence spectra (See SI, explained in detail).



Scheme 1. Mechanism of supramolecular polymerization of *L*-**1** and *D*-**1**; (a) monomeric species, (b) the formation of linear nanorod, and (c) chiral supramolecular polymers with left- or right handed helicity by mechanical stimuli.

Since *L*-**1** and *D*-**1** have a chiral center localized at the alanine moieties, we measured their CD spectra to study the supramolecular chirality (Figures S6, S7, and S8). An *L*-**1** weak positive CD signal at 325 nm was obtained without rotation, which corresponded to the π-π* transition of the *L*-**1** tetraphenylethene moiety. A distinct and drastic enhancement of the CD signal for the negative sign at 275 nm and the positive sign at 325 nm was observed, which was ascribed to the formation of a left-handed (*M*-type) supramolecular polymer characterized by excitonically-coupled helical organization.[28] In contrast, the CD signal of *D*-**1** was exactly the opposite behavior of *L*-**1** (Figures S6B, and S8). This CD signal of *D*-**1** indicates that the tetraphenylethene moiety was orientated in the right-handed (*P*-type) direction. The enhancement of the CD signal of *D*-**1** by the mechanical stimulus showed the same tendency as *L*-**1**, suggesting that the supramolecular chirality induced by the mechanical stimulus was dominated by a stereo-enantiomeric residue. In addition, the CD intensity of *L*-**1** and *D*-**1** was not significantly changed without stirring until 600 min (Figure S6B). In contrast, the CD intensity of *L*-**1** and *D*-**1** linearly increased by rotation at 1,000 rpm and maintained a constant intensity after 240 min (Figure S6B), which indicates that the supramolecular polymerization was accelerated and supramolecular helicity was induced only by the mechanical stimulus. The enhancement of the distinct CD intensity also depended on the rotation speed (Figures S7 and S8). Based on the luminescence and CD observations, we realized that the mechanical stimulus of solution *L*-**1** and *D*-**1** generated not only strong luminescence with an AIE effect but also chiral supramolecular polymerization, which is a rare example of supramolecular polymerization (Scheme 1). Especifically, on the basis of luminescence and CD observations, the lag time in the CD observation was longer than that of luminescence observation. A linear nanorod, which exhibits luminescence with an AIE effect, was formed. However, the molecules in the nanorod were not arranged helically in the initial state. After a certain mechanical stimulus, the nanorod grew into the fiber structure. In this process, the linear molecular arrangement in the nanorod was converted into the helical molecular arrangement during the formation of the fiber structure by mechanical stimulus. Thus, external mechanical stimulus acted as a helical inducer and accelerator during supramolecular polymerization.

To investigate the influence of rotation direction on the handedness and the AIE effects, we observed the luminescence and CD spectral enhancements of *L*-**1** under anticlockwise rotation (Figure S9). The resulting enhancement of the *L*-**1** luminescence was exactly the same obtained from the clockwise rotation. This observation was opposite to that previously reported in the literature,[25,29-31] in which supramolecular helicity was controlled by rotation direction. In previous studies,[25,31-33] researchers investigated the control of helicity of achiral compounds by the rotational direction. The helicity of achiral compounds depended on the rotational direction. However, the helicity of *L*-**1** at the supramolecular level was independent of the stirring direction owing to the chiral alanine moiety. External stimulus is not sufficient to invert helicity to original chirality owing to the steric hindrance effect of the chiral center. Thus, molecular chirality was directly reflected on supramolecular helicity.

As a reference experiment, we observed the luminescence spectral change of **2** composed of glycine moieties instead of alanine moieties under the same condition (Figure S10A). The weak emission band of **2** (2.5×10^{-5} M) was also obtained at 500 nm in the THF without stirring. However, the green emission band did not change to a blue emission even though solution **2** was under strong rotation (1,000 rpm) for 7 days (Figure S10B). These findings indicate that the enantiomeric alanine moiety of *L*-**1** and *D*-**1** plays a critical role in the conversion of the monomer to the chiral supramolecular polymer with a helical arrangement. Because the intramolecular hydrogen bonds of *L*-**1** and *D*-**1** were easily dissociated by the structural steric hindrance owing to the presence of methyl groups. Then, non-intramolecular hydrogen-bonded monomers *L*-**1** or *D*-**1** grew into CPL supramolecular polymers in the chiral direction of alanine by intermolecular hydrogen bonding.

To gain an insight into the morphological changes of the self-assemblies over the time of mechanical stimulation, we observed the morphologies of supramolecular polymers *L*-**1** and *D*-**1** using atomic force microscopy (AFM, Figures 2 and S11–12). The AFM image of *L*-**1** with a green emission could not be clearly obtained. However, the AFM image of *L*-**1** with a blue emission, obtained at a rotational speed of 1,000 rpm showed the nanorod-like structure with uniform length of ca. 0.3 μm after 20 min of rotation (Figures 2a and S11), and was observed a short fiber-like structure with uniform length of ca. 0.8 μm and a diameter of ~70 nm after 60 min of rotation (Figures 2b and S11). After stirring the solution for 120 min, the long fiber-like structure with clear left-handed helicity was observed. More interestingly, the fiber lengths were controlled by rotational time (Figure S11), which was the first example for the control of fiber length by rotational times. These findings suggest that the degree of polymerization can be controlled by external mechanical stimulus. Thus, the fiber tuned by mechanical stimulus is useful as seed and building block in living supramolecular block copolymerization. In contrast, the AFM image of *D*-**1** with a blue emission showed a right-handed helical fiber (Figure S12). These observations suggest that the fiber-like structure of the supramolecular polymer with blue emission was generated by a nucleation-elongation mechanism, as demonstrated by the time and temperature dependent CD spectral changes (Figures 1B and S13). Furthermore, interestingly, the length of the supramolecular fibers was shortened by the mechanical stimuli strength increased at the same luminescence intensity (I = 500), which indicates that the supramolecular polymerization was accelerated by the rapid and more nucleation formation in solution by increasing mechanical strength. (Figure S14). Additionally, the ~70 nm diameter left-handed (*M*-type) fibers were obtained by anticlockwise rotation (Figure S15). This result again confirms that the handedness of the supramolecular polymer *L*-**1** was not determined by the external stimulus-like rotation direction.

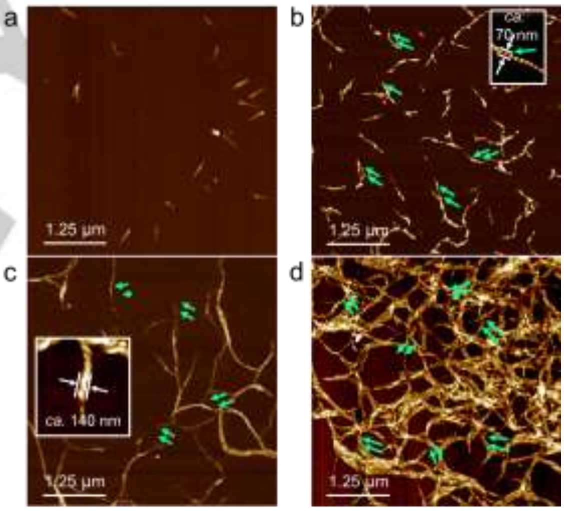


Figure 2. Time dependent AFM images of *L*-**1** (2.5×10^{-5} M) in THF; (a) 20 min, (b) 60 min, (c) 120 min, and (d) 240 min under 1,000 rpm.

^{1}H NMR spectra changes of *L*-**1** by change of temperature were observed (Figure S16). Two N-H proton peaks of *L*-**1** with blue emission, prepared by stirring for 1 day, were observed at 7.79 and 7.64 ppm at 298 K, respectively, which were shifted 0.16 and 0.17 ppm downfield compared to those at 333 K. These chemical shifts were clear evidence for the dissociation of the intermolecular H-bonds (See SI: explained in detail). In addition, the -NH of *L*-**1** with green emission showed bands at 3583 and 3507 cm^{-1} and **2** showed bands at 3550 and 3482 cm^{-1}, respectively (Figure S17), which corresponds to the non-hydrogen-bonded and intramolecular hydrogen-bonded -NH groups. In contrast, the -NH band of *L*-**1** with blue emission shifted

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to 3294 cm^{-1}, which was indicative of the formation of intermolecular hydrogen-bonding interactions between the amide groups of *L*-**1**. This is clear evidence that the mechanical stimulus accelerated the chiral supramolecular polymerization by the dissociation of the intramolecular hydrogen-bonds through the formation of intermolecular hydrogen-bonds.[32,33]

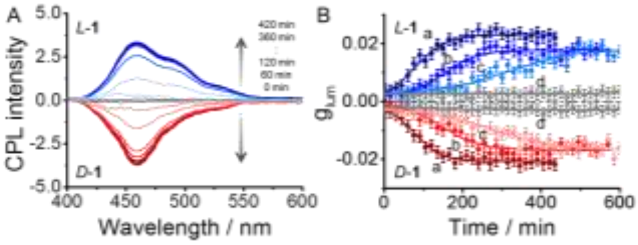

Figure 3. (A) Time dependent CPL spectra of *L*-**1** (blue line) and *D*-**1** (red line) (2.5×10^{-5} M) with 1,000 rpm in THF. (B) Plot of time dependent g_{lum} factor of *L*-**1** and *D*-**1** with 1,000 rpm at 455 nm in THF; (a) 1,000, (b) 600, (c) 200, (d) 0 rpm for *L*-**1** (positive signals) and *D*-**1** (negative signals), respectively.

We then studied the effects of mechanical stimulus on the CPL properties using different rotation rates (i.e. 200, 600, and 1,000 rpm) under the same solvent conditions as the CD observations, namely a mechano-CPL effect. The changes in the CPL spectra of both *L*-**1** and *D*-**1** at different rotational speeds are presented in Figures 3 and S18–19. The mirror-image CPL signals for the two enantiomers at 455 nm at the same rotation rate of 1,000 rpm were observed in the *L*-**1** and *D*-**1** samples. The helicity of the CPL signals were the same as the CD signals, which indicates that the CPL helicity of the supramolecular polymers originated from the molecular chirality localized at the alanine moiety. More interestingly, very weak CPL signals changes of *L*-**1** and *D*-**1** were observed during stirring in the initial stage (Figure S19), which were ascribed to the intramolecular hydrogen-bonds of *L*-**1** and *D*-**1**. However, the CPL signals of *L*-**1** and *D*-**1** increased almost linearly after a constant rotational time, as shown by the CD observations, and the maximum CPL signals were dependent to the rotational speed. These findings suggested that the well-ordered helical molecular arrangement of *L*-**1** and *D*-**1** molecules in the chiral supramolecular polymerization was controlled by the mechanical stimulus. The magnitude of the CPL can be evaluated by the luminescence dissymmetry factor ($|g_{lum}|$), which is defined as $g_{lum} = 2 \times (I_L - I_R)/(I_L + I_R)$, where I_L and I_R refer to the intensity of the left- and right-handed CPL, respectively. The dissymmetry factors ($|g_{lum}|$) of the CPL signals of *L*-**1** and *D*-**1** with different rotation times (i.e. 0, 60, 120, 180… and 420 min) also increased with increasing rotation time, as shown in Table S1. These results indicate that the chiral supramolecular polymerization required sufficient mechanical stimulation time to form the helical molecular arrangement with the intermolecular hydrogen-bonding interactions and CH-π stacking. The dissymmetry factor obtained at 1,000 rpm was relatively large compared with the factors reported in gel[34] which indicates that the left- and right-handed supramolecular polymerization was controlled by the strength of the mechanical stimulus.

In conclusion, we have demonstrated CPL supramolecular polymerization based on a tetraphenylethene core bearing alanine moieties by tuning the rotational speed. The dissymmetry factors ($|g_{lum}|$) of the CPL signals of *L*-**1** (*D*-**1**) were successfully controlled by the external mechanical stimulus; this is the first example of the control of the dissymmetry factor of the CPL signals. The molecules exhibited tunable emission by changing from green to blue in solution. The chiral supramolecular polymers exhibiting the blue emission by AIE effect were generated by a typical nucleation-elongation pathway. More interestingly, the important enhancement of the CD and CPL signals in the *L*-**1** and *D*-**1** solutions was observed when the external stimulus was used compared with when it was not used, to reach high dissymmetry ($|g_{lum}|$) values of $\pm 2.2 \times 10^{-2}$ under a rotational speed of 1,000 rpm. Furthermore, the CD and CPL signals were able to be finely tuned using different strengths and durations of the external mechanical stimulus. Therefore, we believe that this unique mechano-responsive CPL will provide a distinctive insight into the design of functional chiroptical living supramolecular polymers based on emissive chiral molecules.

Acknowledgements

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Keywords: • Supramolecular Polymerization • Circularly Polarized Luminescence • Helicity • AIE Effect • Mechano-Responsive Material

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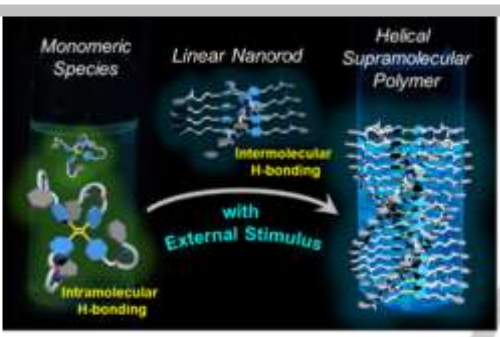
Controlled Circularly Polarized Luminescence: These results imply that the CPL signals were tuned by the strength of the external mechanical stimulus.



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