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# Unpolarized-Light-Driven Amplified Chiroptical Modulation Between Chiral Aggregation and Achiral Disaggregation of an Azobenzene-*alt*-Fluorene Copolymer in Limonene

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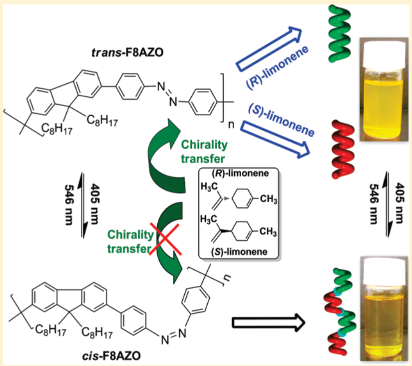
S *Supporting Information*

**ABSTRACT:** A *trans*−*cis* photoisomerizable achiral polymer, poly[(9,9-di-*n*-octylfluorenyl-2,7-diyl)-*alt*-4,4′-azobenzene] (**F8AZO**), was designed. The chirality of (*S*)- and (*R*)-limonene used as a solvent allowed for the generation of optically active **F8AZO** aggregates, revealing intense circular dichroism (CD) signals in the visible region. The reversible chiroptical response was achieved upon alternating photoirradiation at 405 nm (*trans*-form) and 546 nm (*cis*-form). This ability originated from the switching between the *trans*-origin aggregation and *cis*-origin disaggregation of **F8AZO** in the limonene−2-propanol−chloroform tersolvent.



## INTRODUCTION

Incoherent unpolarized sunlight plays key roles in the migration and delocalization of photoexcited energy in optically active aggregates containing large numbers of chlorophyll molecules surrounded by an aqueous fluid (stroma) of chloroplasts.[1] Sunlight can also drive the *trans*−*cis* isomerization of *p*-coumaric acid moieties surrounded by protein shells (photoactive yellow protein).[2] These chiroptical properties are modulated in response to changes in osmotic pressure, cations, sunlight intensity, and temperature. On the other hand, reversible light-driven chiroptical switching is of current interest due to its useful application in optical memory, molecular motors, and molecular machines.[3]

Among the several photoisomerizable molecules that exist, azobenzene (**AZO**) has proven to be a useful building block in chiroptical switching due to the reversibility between its *trans* and *cis* states. The drastic changes in its dipole moment between 0 to 3 D and in molecular shape between extended coplanar and twisted bent forms with a reduction of the C4−C4′ distance from 9.0 to 5.5 Å result in altered solubility and free volume properties.[4,5] The reversible characteristics of **AZO** upon photoirradiation enables the modulation of the degree of intra- and interchain interactions, facilitating control over photodriven aggregation/disaggregation processes of $\pi$-conjugated polymers in solution.[5,6] Although several studies on chiroptical switching properties, featuring **AZO**-containing small molecules,[4] oligomers,[5a,b] and polymers,[5c−g] have already been performed, these systems inevitably require a multistep synthesis and expensive chiral sources with high *ee*. The change in the magnitude of optical activity in these polymers, however, is not so remarkable in response to *trans*−*cis* photoisomerization of **AZO** units in most cases.[7] Hence, a more general and versatile **AZO**-based chiroptical switching system may be desirable.

Solvent chirality transfer has been shown to be an efficient and versatile protocol in generating ambidextrous chromophoric aggregates from achiral chromophoric polymers.[8] Recently, we demonstrated the production of aggregates with intense circular dichroism (CD) signals from several achiral fluorene-containing $\pi$-conjugated polymers with the help of solvent chirality transfer from (*R*)-limonene (**1*R***) and (*S*)-limonene (**1*S***) in the dark.[8e,f]

Learning from the above photo- and environment-responsive biomolecular and artificial systems, we demonstrate the first example of a chiroptical switching **AZO**-containing $\pi$-conjugated polymer with the help of limonene chirality transfer at the photoexcited and/or ground states. The idea is that the incorporation of photoisomerizable **AZO** groups into the poly(di-*n*-octylfluorene) backbone as alternating units (**F8AZO**, $M_n = 7770$ g mol$^{-1}$, $M_w/M_n = 2.62$, Figure 1) surrounded by an organic chiral fluid enables the cooperative and efficient control of chiral aggregation and achiral disaggregation induced by reversible *trans*−*cis* photoisomerization of **AZO** units in **F8AZO**.

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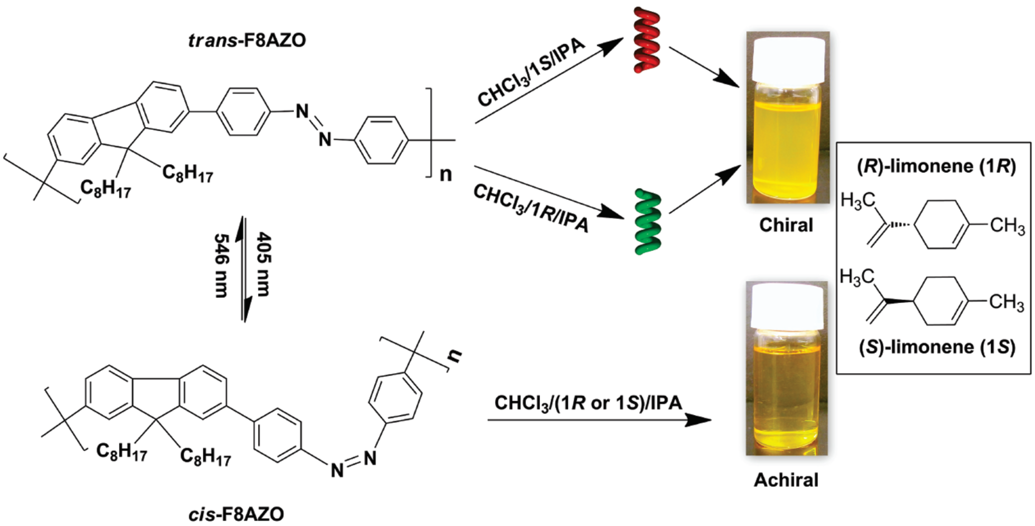


**Figure 1.** Schematic illustration of unpolarized-light-driven chiroptical switching in $CHCl_3$/(**1*R*** or **1*S***)/IPA (0.3/1.5/1.2, v/v/v). In *trans*-**F8AZO**, chiral aggregation occurred as a bright yellow and turbid solution, while the formation of nonaggregated *cis*-**F8AZO** was seen as a yellow transparent solution. **F8AZO**: poly[(9,9-di-*n*-octylfluorenyl-2,7-diyl)-*alt*-4,4′-azobenzene]. **1*R***: (*R*)-limonene. **1*S***: (*S*)-limonene.

## EXPERIMENTAL SECTION

**General Procedures.** Spectroscopic grade chloroform, methanol, hexane, ethanol, and 2-propanol (Wako, Japan) were used to prepare the polymer solutions and for measurements. Anhydrous THF and benzene were purchased from Wako and generally used without further purification. (*S*)-Limonene (**1*S***) and (*R*)-limonene (**1*R***) (Chart S1, Supporting Information) were obtained from Aldrich and purified by distillation under reduced pressure prior to use. (*R*)-form: $[\alpha]^{25}{}_{589}$ = +100.78° (neat), > 99.0% *ee*. (*S*)−form: $[\alpha]^{25}{}_{589}$ = −100.97° (neat), > 99.0% *ee*. All other analysis grade chemicals were purchased from TCI (Tokyo, Japan) and used as received. The CD spectra of the solutions were recorded on a JASCO J-725 spectropolarimeter equipped with a Peltier-controlled housing unit using a SQ-grade cuvette, with a path length of 10 mm (and a scanning rate of 100 nm/min, bandwidth of 1 nm and response time of 1 s, using a single accumulation) at 25 °C. UV−vis spectra were measured independently on a JASCO UV-570 UV−vis−NIR spectrophotometer at 25 °C (with a scanning rate of 100 nm/min, bandwidth of 2 nm and response time of 1 s). Fluorescent spectra were measured on a JASCO FP-6600 spectrofluorometer (a scanning rate of 200 nm/min, bandwidth of 2 nm and response time of 1 s) at 25 °C. $^1H$ and $^{13}C$ NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz for $^1H$, 100.40 MHz for $^{13}C$). All spectra were obtained in $CDCl_3$ at 25 °C. Chemical shifts are given in ppm and are referenced to $SiMe_4$ ($\delta$ 0.00; $^1H$, $^{13}C$). The weight-average molecular weight ($M_w$), number-average molecular weight ($M_n$), and polydispersity index ($PDI = M_w/M_n$) were evaluated using gel permeation chromatography (GPC) on a Shimadzu A10 instrument with PLgel (Varian) 10 $\mu$m mixed-B as the column and HPLC-grade THF as the eluent at 40 °C (calibrated with polystyrene standards). Elemental analyses were performed on a PE2400II Series instrument (Perkin-Elmer). High-resolution mass spectrometry (HRMS) was performed using positive electrospray ionization ($m/z$) on a JMS-700 (JEOL). Wide-angle X-ray diffraction (WAXD) data were collected on a Rigaku R-AXIS-IV wide-angle X-ray diffractometer (Ni-filtered Cu*K*α, 45 kV, 50 mW) and analyzed by Rigaku automatic X-ray imaging software. HR-TEM images were obtained with a JEOL JEM-3100FEF electron microscope (accelerating voltage of 300 kV, bright-field image).

**Synthesis of 4,4′-Dibromoazobenzene.**[6c,10] Manganese dioxide (10.44 g, 0.12 mol) and 4-bromoaniline (3.44 g, 0.02 mol) were added to 100 mL of dry benzene at room temperature. The solution was stirred for 22 h at room temperature and then at 60 °C for 24 h. After filtration, the crude product was isolated by evaporating the solvent. The product was recrystallized from chloroform to give a yellow plate-like crystal (2.97 g, 86%). $^1H$ NMR (399.65 MHz, $CDCl_3$): $\delta$ 7.66 (s, 2H), 7.80 (s, 2H). $^{13}C$ NMR (100.40 MHz, $CDCl_3$): $\delta$ 151.3, 132.6, 125.9, 124.5. Anal. Calcd for $C_{12}H_8Br_2N_2$: C, 42.39; H, 2.37; N, 8.24. Found: C, 42.36; H, 2.12; N, 8.16. HR−MS (EI) calcd for $C_{12}H_8Br_2N_2$ ($[M]^+$), 339.9034; found, 340.0021.

**Preparation of Poly[(9,9-di-*n*-octylfluorenyl-2,7-diyl)-*alt*-4,4′-azobenzene] (F8AZO) (Chart S1, Supporting Information).**[11] The reagents 4,4′-dibromoazobenzene (0.26 g, 0.765 mmol), 9,9-dioctylfluorene-2,7-diboronic acid bis(1,3-propanediol)ester (0.427 g, 0.765 mmol), and $(PPh_3)_4Pd(0)$ (8.84 mg, 1 mol %) were dissolved in a mixture of THF (5 mL) and 2 M $Na_2CO_3$ (3.33 mL) under nitrogen atmosphere. The solution was maintained at 80 °C with vigorous stirring for 72 h. The whole mixture was poured into a mixture of methanol and water (500 mL, $CH_3OH/H_2O$ = 10/1 (v/v)). The precipitate was recovered by filtration and washed with a large amount of water. The resulting precipitate was washed for 72 h in a Soxhlet extracting apparatus using acetone to remove oligomers and catalyst residues. The resulting polymer produced a yellow solid (0.45 g, 65.5%). $M_n$ = 7 770 g mol$^{-1}$, $M_w/M_n$ = 2.62. $^1H$ NMR (399.65 MHz, $CDCl_3$): $\delta$ 7.60−8.10 (14 H), 1.91−2.20 (4H), 0.70−1.25 (30 H). $^{13}C$ NMR (100.40 MHz, $CDCl_3$): $\delta$ 152.10, 152.01, 144.25, 140.73, 139.35, 132.50, 127.95, 126.43, 124.53, 123.64, 121.66, 120.47, 55.60, 40.53, 31.92, 30.14, 29.35, 24.02, 22.75, 14.21. Anal. Calcd for $(C_{41}H_{48}N_2)_n$: C, 86.49; H, 8.44; N, 4.92. Found: C, 84.81; H, 8.48; N, 4.70.

**Preparation of Optically Active F8AZO Aggregates.** The typical procedure for the production of **F8AZO** aggregates in a mixed chloroform/limonene/2-propanol was described. First, 1.5 mL of **1*R*** was added to 0.3 mL of a chloroform stock solution containing **F8AZO** ($[\text{repeating unit}]_0$ = 3.5 × $10^{-5}$ mol L$^{-1}$) in a SQ-cuvette, which was placed in the Peltier apparatus of a JASCO J-725 spectropolarimeter at 25 °C and stirred clockwise for 30 s at 1000 rpm. The addition of 1.2 mL 2-propanol to the above solution at 25 °C resulted in a yellowish turbid solution of **F8AZO** aggregates dispersed in the mixed solvent. After being stirred for 120 s, this solution was used for CD/UV−vis spectroscopic measurements. **F8AZO** aggregates in other mixed solvents were obtained in a similar way.

**Photoisomerization of F8AZO Solution.** Irradiation was conducted using a 500-W high-pressure mercury lamp (Ushio (Tokyo,

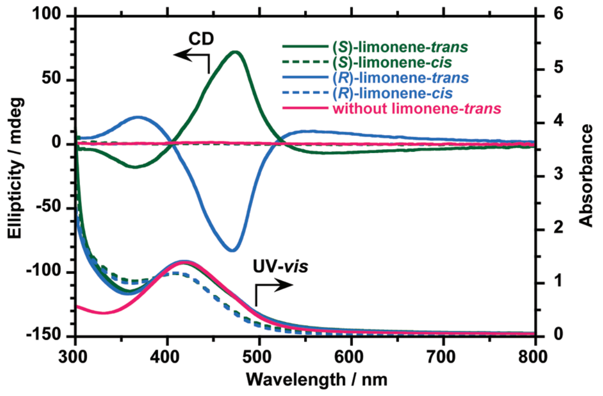


**Figure 2.** Changes in CD and UV−vis spectra of **F8AZO** aggregates ($3.5 \times 10^{-5}$ mol $L^{-1}$) in ($CHCl_3$/(**1*R*** or **1*S***)/IPA (0.3/1.5/1.2, v/v/v)) or ($CHCl_3$/IPA (1.7/1.3, v/v)) at room temperature. **F8AZO**: poly[(9,9-di-*n*-octylfluorenyl-2,7-diyl)-*alt*-4,4′-azobenzene]. **1*R***: (*R*)-limonene. **1*S***: (*S*)-limonene.

Japan), Optiplex BA-H501 and USH-500SC2), and the wavelengths (405 and 546 nm) were selected with the aid of narrow bandpath filters (Sigma Koki, Tokyo, Japan). The irradiation intensities were 159 $\mu$W $cm^{-2}$ at 405 nm and 589 $\mu$W $cm^{-2}$ at 546 nm, respectively (Ophir Optronics with Nova with photodiode head PD300-UV (Tel-Aviv, Israel)).

**Gaussian03 Calculation.**[12] Potential surface energies of **FL-AZO-FL**, which is **F8AZO** model oligomer, and **AZO** small molecule (Chart S2, Supporting Information) were performed using Gaussian03 program running on an Apple iMac (IntelCoreDuo2, 2.0 GHz, 4GB memory, MacOS ver.10.4.11). The geometries of **FL-AZO-FL** were optimized by the PM3-MM level calculation using default standard parameters as a function of dihedral angles between fluorene and azobenzene rings ($C_1-C_2-C_3-C_4$) varying from *anti-* (180°) to *syn*-forms (0°) with 15° intervals. Potential energy surface of *trans-* and *cis*-forms of **FL-AZO-FL** and **AZO** were obtained by Gaussian03 (PM3-MM with initial standard parameters) as a function of dihedral angle of $C_5-N_1-N_2-C_6$ from *trans-* (180°) to *cis*-like forms (60°) with 15° intervals, while dihedral angles between fluorene and azobenzene rings was fixed to 45°. Simulated CD spectra of several **FL-AZO-FL** and **AZO** conformers were obtained using the TD-DFT (B3LYP, 3-21G basis set) protocol.

## RESULTS AND DISCUSSION

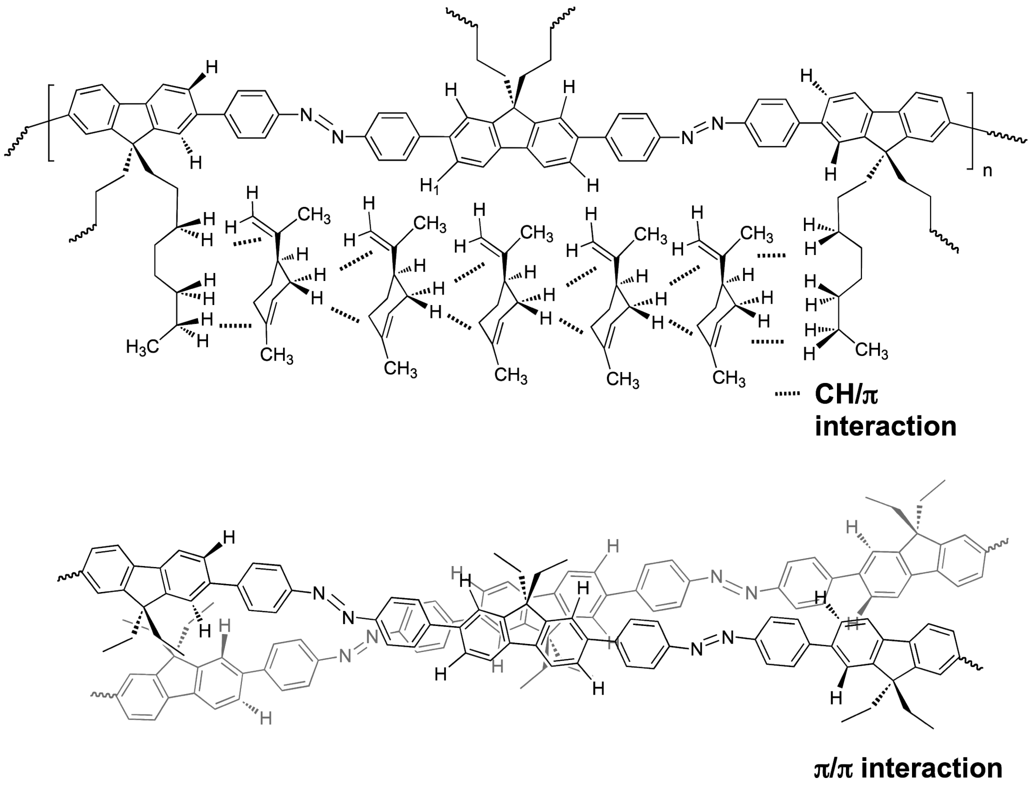
Poly[(9,9-di-*n*-octylfluorenyl-2,7-diyl)-*alt*-4,4′-azobenzene] (**F8AZO**) can undergo reversible *trans*−*cis* photoisomerization in $CHCl_3$ upon alternating photoirradiation with 405 nm (159 $\mu$W $cm^{-2}$) and 546 nm (589 $\mu$W $cm^{-2}$) light (Figures S1 and S2, Supporting Information): 405 nm for *trans* with the allowed $\pi-\pi^*$ transition and 546 nm for *cis* with the forbidden $n-\pi^*$ transition. Although *trans*-**F8AZO** in chloroform excited at 380 nm can emit at 430 nm with a high quantum efficiency ($\Phi$ ~12%) and lifetime of 1.41 ns, **AZO** in chloroform can emit at 430 nm, exhibiting a high $\Phi$ ~25% and lifetime of 1.43 ns, as evaluated by 1,9-diphenylanthracene as a reference (Figure S3, Supporting Information). However, a suspension of *trans*-**F8AZO** aggregates was nonemissive.

The optically active aggregates of *trans*-**F8AZO** were successfully produced by the limonene chirality transfer protocol ($CHCl_3$/**1*R*** or **1*S***/IPA = 0.3/1.5/1.2, v/v/v) (Figures 1 and 2). Almost mirror-image CD spectra of *trans*-**F8AZO** as the aggregate form were obtained when **1*S*** was replaced by **1*R***. However, no detectable CD signals emerged in the $\pi-\pi^*$ transition region when *trans*-**F8AZO** aggregates were dispersed in a mixed $CHCl_3$/IPA (1.7/1.3, v/v) without **1*R*** and **1*S***, even though a very similar broad UV−vis spectrum in a turbid solution appeared. The proper choice of a cosolvent and appropriate volume fraction in a polar chiral-achiral cosolvent is very important to efficiently produce CD-active $\pi$-conjugated polymer aggregates.[8] In five poor solvent/$CHCl_3$/**1*R*** = 1.2/0.3/1.5 (v/v/v) mixtures that were tested, the absolute CD magnitude at 450−500 nm decreased in the order IPA > *n*-propanol > methanol > ethanol ≫ *n*-hexane (Figure S4, Supporting Information). CD signals completely disappeared in hexane. The maximum CD amplitude of *trans*-**F8AZO** aggregates varied greatly with the relative volume fraction of **1*R*** and IPA (Figure S5a, Supporting Information). By changing the volume ratio of **1*R***/IPA (keeping $CHCl_3$ 0.3 mL constant), **1*R***/IPA = 1.5/1.2 (v/v) was found to provide the maximum absolute CD amplitude. When the volume fraction of **1*R*** and IPA exceeds 1.5/1.2 (v/v), the absolute CD amplitude decreased with an decrease in poor IPA solvent resulting from the decrease of $\pi-\pi$ stacking ability, which was proven by their UV−vis spectra (Figure S5b, Supporting Information). When the volume fraction of **1*R*** and IPA was less than 1.5/1.2 (v/v), the apparent decrease in CD amplitude is attributable to the production of loose precipitates. Interestingly, this system did not show a marked majority-rule effect of chiroptical amplification (Figure S6, Supporting Information). The similar *ee* dependency of the chiral solvent effect was also recently reported.[8e,f]

Photoinduced chiral recognition by using polymers endowed with main chain and/or **AZO** pendant groups has been achieved, though these polymers often require a multistep synthesis with expensive chiral source materials with high *ee*.[5c−g] Most interestingly, in $CHCl_3$/**1*R*** or **1*S***/IPA (0.3/1.5/1.2, v/v/v), *cis*-**F8AZO** solution was almost transparent, as compared with that of *trans*-**F8AZO**, as shown in Figure 1. Furthermore, any CD signal of *cis*-**F8AZO** in the presence of either **1*R*** or **1*S*** was both not detected (Figure 2). A helically $\pi-\pi$ stacked aggregation of the *trans*-**F8AZO** with a preferential twist sense induced by the limonene chirality in the ground and/or photoexcited states should be responsible for a greatly amplified CD signals. A possible model of the optically active **F8AZO** aggregates was proposed as presented in Scheme 1. These led to the idea that the aggregation-and-disaggregation characteristic of **F8AZO** is reversibly controlled by the *trans*−*cis* photoisomerizable **AZO** units in the presence of limonene.

Changes in the UV−vis spectra of *cis*-**F8AZO** under 546 nm light irradiation confirmed the occurrence of *cis-to-trans* photoisomerization (546 nm: forbidden weaker $n-\pi^*$ and 405 nm for allowed intense $\pi-\pi^*$ absorptions, respectively) in $CHCl_3$/**1*R*** or **1*S***/IPA (0.3/1.5/1.2, v/v/v) (Figure S7, Supporting Information).[6] Parts a and c of Figure S7 (Supporting Information) show that the *cis-to-trans* photoisomerization process is almost complete within 1 min of 546 nm light irradiation in the presence of **1*R*** and **1*S***. The $\pi-\pi^*$ absorption at 420 nm progressively decreased by 18% because the aggregation became stronger with time. The CD signals of the *trans*-**F8AZO** aggregates began to appear at ~2 min and reached a maximum value upon prolonged irradiation (60 min), when the nonaggregate form of *cis*-**F8AZO** in the chiral tersolvent was treated with 546 nm light irradiation (Figure S8, parts a and b, Supporting Information). The absolute CD magnitude increased with irradiation time and had a visible band slightly red-shifted by ~30 nm, which indicated that $\pi-\pi^*$ aggregation had become more intense with irradiation time along with *cis*-to-*trans* photoisomerization. In contrast, the

**Scheme 1. Proposed Models of (Top) Plural Intermolecular Chiral CH/*π* Interactions between *n*-Octyl Chains of F8AZO and Limonene Molecules and (Bottom) Plural Intermolecular *π*/*π* Interactions between F8AZO in a Helically Stacked *J*-Aggregate Form (F8AZO: Poly[(9,9-di-*n*-octylfluorenyl-2,7-diyl)-*alt*-4,4′-azobenzene])**



absolute CD magnitude increased with time (without irradiation) after 2 min of irradiation with 546 nm light in the chiral tersolvent (Figure S9, Supporting Information). However, the CD maximum values were both lower than those with continuing irradiation. The reason for this may be that the continuing irradiation is helpful for the aggregation of *trans*-**F8AZO** in the tersolvents.

The reversibility of the CD signals generated from **F8AZO** in the tersolvent was verified by alternating irradiating with 405 and 546 nm light for 10 min intervals. Six switching cycles were tested, and the results are given in Figure 3. Here the Kuhn's dimensionless parameter, $g_{CD}$ value, defined as $\Delta\varepsilon/\varepsilon$ at 460 nm, is used to discuss the measure of chirality.

The absolute $g_{CD}$ value was reversibly converted between almost zero and $\sim 1 \times 10^{-3}$ in response to the *trans*−*cis* photoisomerization of **F8AZO**. The responding time on a solution level is relatively slow because the power intensity of the light source was limited to only 159 $\mu$W cm$^{-2}$ at 405 nm and 589 $\mu$W cm$^{-2}$ at 546 nm due to unfocused beam of a high-pressure Hg-light source, and massive polymer chains may have a long diffusion time in solution. However, the former issue should be overcome properly with the help of recently commercialized high-power blue-violet laser diode (LD) (405−410 nm, up to ~300 mW, CW and pulse-mode operations) and the forthcoming high-power green LD (500−531 nm, CW and pulse-mode operations). The latter would also be solved by the adoption of the optically confined trench-and-spacer architecture based on a gel-like polymer composite film including limonenes and liquid crystals with the help of "photochromic command surface concept".[3m−q]

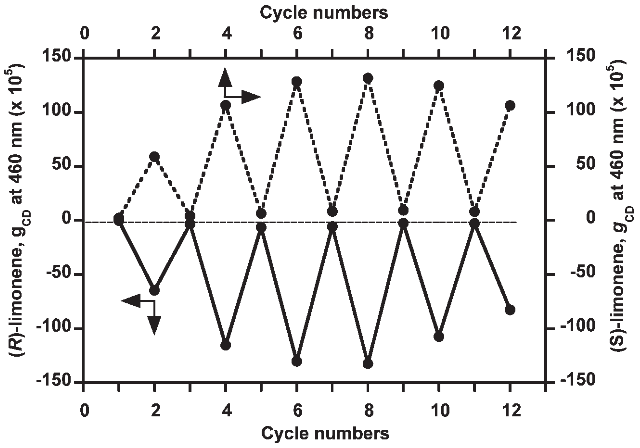


**Figure 3.** Change in the $g_{CD}$ value at 460 nm upon alternating photoirradiation cycles with 405 and 546 nm light in $CHCl_3$/(**1*R*** or **1*S***)/IPA (0.3/1.5/1.2 (v/v/v). Irradiation time: 10 min. A $CHCl_3$ solution of **F8AZO** ($3.5 \times 10^{-4}$ mol L$^{-1}$) was irradiated for 30 min with 405 nm light to obtain the *cis*-**F8AZO** solution. **F8AZO**: poly[(9,9-di-*n*-octylfluorenyl-2,7-diyl)-*alt*-4,4′-azobenzene]. **1*R***: (*R*)-limonene. **1*S***: (*S*)-limonene.

In *trans*-form, the $|g_{CD}|$ value became intense due to the successful transfer of **1*R*** or **1*S*** to **F8AZO** aggregates. In sharp contrast, the $|g_{CD}|$ value in *cis*-form became very weak. We assume that the aggregates disaggregated and limonene molecules were released from the aggregates. However, the $|g_{CD}|$

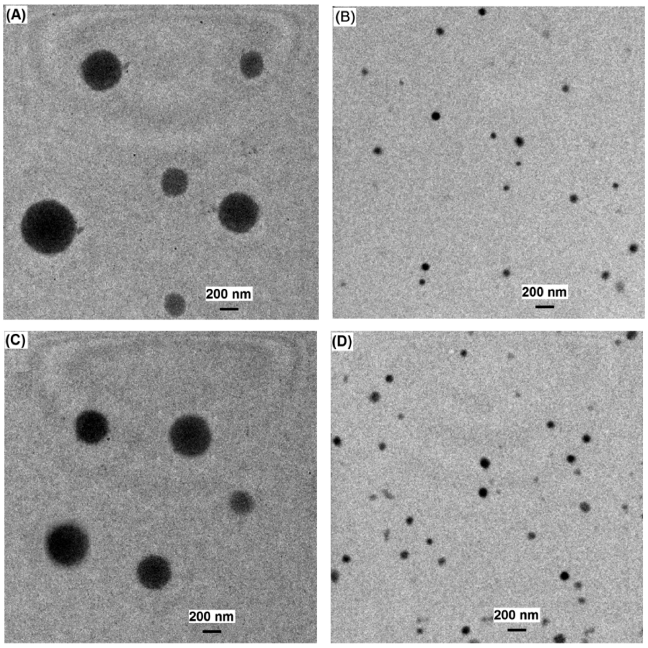


**Figure 4.** HR-TEM images of *trans*- and *cis*-**F8AZOs** in $CHCl_3$/(**1*R*** or **1*S***)/IPA (0.3/1.5/1.2 (v/v/v): (A) *trans*-**F8AZO-1*R***; (B) *cis*-**F8AZO-1*R***; (C) *trans*-**F8AZO-1*S***; (D) *cis*-**F8AZO-1*S***. **F8AZO**: poly[(9,9-di-*n*-octylfluorenyl-2,7-diyl)-*alt*-4,4′-azobenzene]. **1*R***: (*R*)-limonene. **1*S***: (*S*)-limonene.

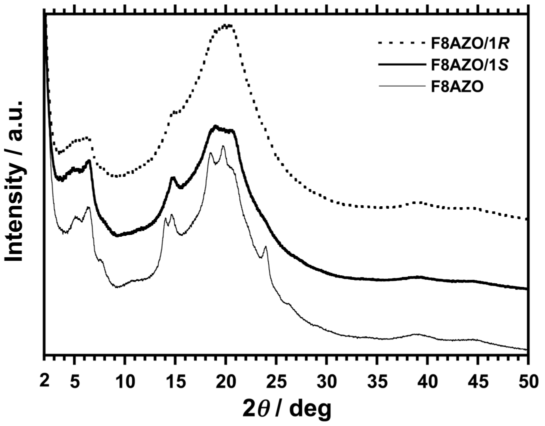


**Figure 5.** WAXD data of *trans*-**F8AZO** aggregates (dotted line; **F8AZO-1*R***, thick solid line; **F8AZO-1*S***, thin solid line; **F8AZO**) produced with **1*R*** and **1*S*** and without limonene. **F8AZO**: poly[(9,9-di-*n*-octylfluorenyl-2,7-diyl)-*alt*-4,4′-azobenzene]. **1*R***: (*R*)-limonene. **1*S***: (*S*)-limonene.

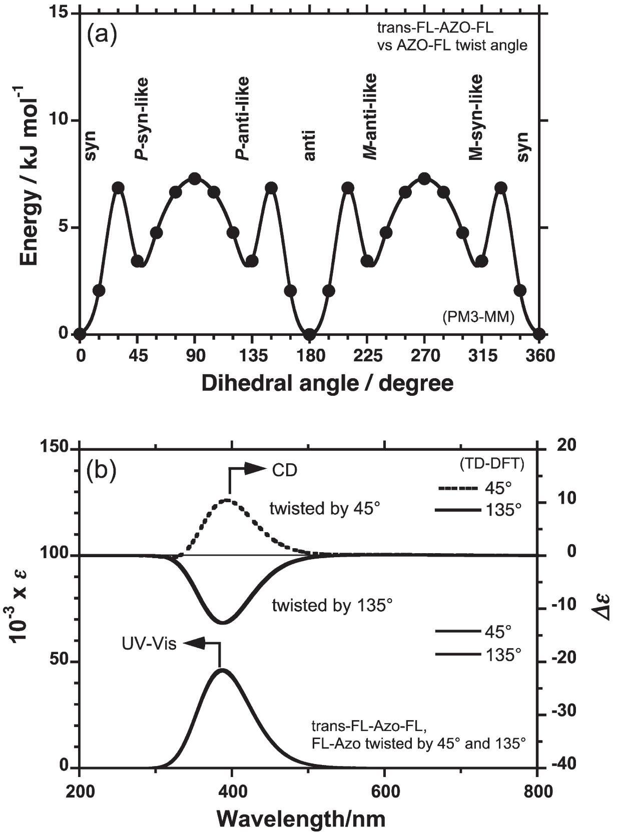


**Figure 6.** (a) Potential energy surface of *trans*-**FL-AZO-FL** (**F8AZO** model oligomer) as a function of **AZO-FL** dihedral angle ($C_1$–$C_2$–$C_3$–$C_4$, Chart S2, Supporting Information). (b) Simulated UV–vis and CD spectra of *trans*-**FL-AZO-FL** (**AZO-FL** dihedral angle 45° and 135°). **FL-AZO-FL**: Fluorene–azobenzene–fluorene.

value of *cis*-**F8AZO** is initially slightly weak but tends to increase by twice its value and reach a constant $|g_{CD}|$ value. A possible explanation for this may be an incomplete transformation from *trans* to *cis* (and *cis* to *trans*) forms during each cycle, as evidenced by their UV–vis spectra (Figure S10, Supporting Information). Although we attempted to a prolong irradiation time (~30 min) for each cycle, but $|g_{CD}|$ values of *cis*-**F8AZO** for each cycle were similar to the above one. The decrease in the absolute $g_{CD}$ values of *trans*-**F8AZO** after four cycles is ascribed to the production of very few precipitates. The present results may be applicable to other similar **AZO**-containing π-conjugated polymers and oligomers in the future. An advanced design of **F8AZO** derivatives, revealing a large $|g_{CD}|$ value, is currently in progress.

The morphology of **F8AZO** aggregates in the mixed solvent ($CHCl_3$/(**1*R*** or **1*S***)/IPA = 0.3/1.5/1.2 (v/v/v) was observed by HR–TEM. Samples were prepared by casting a drop of sample solution onto carbon-coated copper microgrid. As shown in Figures 4 and S11 (Supporting Information), in both cases of **1*R*** and **1*S***, the *trans*-aggregates were ca. 200–500 nm in diameter, conversely, the *cis*-aggregates were only ca. 50 nm, which is smaller than $^1/_4$–$^1/_{10}$ of the *trans*-form. The difference of aggregate sizes between *trans*- and *cis*-forms was due to that π–π stacking ability of *trans*-form was much stronger than that of *cis*-form as evidenced by Figure 1.[6b−d] The different π–π stacking ability between *trans*- and *cis*-forms are responsible for the reversibility of the CD signals as discussed above.

Recently, poly(9,9-di-*n*-alkylfluorene) derivatives are found to assembly into π–π stacking structures with the help of the poor solvent revealed by small-angle X-ray scattering and wide-angle X-ray scattering techniques.[8e,f,9] To elucidate the effect of limonene on CD-active *trans*-**F8AZO** particle growth, wide-angle X-ray diffraction (WAXD) data were collected, as given in Figure 5. The *trans*-particles produced without limonene showed eight major scattering peaks with a relatively narrow width, suggesting a semicrystalline structure. However, the *trans*-particles produced with **1*R*** and **1*S*** adopted a less-crystalline structure revealed by several broader scattering peaks. The *d*-spacings of *n*-octyl side chains in **F8AZO-1*R*** and **F8AZO-1*S*** were 13.71 Å ($2\theta = 6.44°$) and 13.66 Å ($2\theta = 6.46°$), respectively, and 13.83 Å ($2\theta = 6.39°$) in **F8AZO** without limonene. The *d*-spacings between main chains of **F8AZO-1*R*** and **F8AZO-1*S*** were 4.65 Å ($2\theta = 19.08°$) and 4.71 Å ($2\theta = 18.85°$), respectively, and 4.48 Å ($2\theta = 19.76°$) in **F8AZO** without limonene, respectively. These considerable differences might be closely related to the efficient production of CD-active *trans*-**F8AZO** aggregates.

Potential energy surface (PES) calculation of *trans*-**F8AZO** model oligomer (**FL-AZO-FL**, Chart S2, Supporting Information) as a function of **AZO-FL** linkage dihedral angle calculated by Gaussian03 (PM3-MM) suggested that *trans*-**F8AZO** may have achiral *anti*- and *syn*-forms (global minima), and *anti*- and *syn*-like forms with *P*- and *M*-twisted forms (local minima) (Figure 6a). Difference in PES is only 3.5 kJ mol$^{-1}$. Barrier heights among *anti-*/*syn-* and *P-anti*/*P-syn-*/*M-anti*/*M-syn*-like forms are only 3.0−7.0 kJ mol$^{-1}$. These small differences would enable to rapid change in its conformation, in response to photo/thermal-isomerization in the presence of the limonene chirality. Simulated CD spectra (TD-DFT, B3LYP, 3-21G basis set) of *trans*-**FL-AZO-FL** with dihedral angles 45° and 135° of **AZO-FL**, the sign of Cotton CD spectra at 45°-(315°) and 135° (225°) are the opposite (Figure 6b). This infers that the observed CD sign of *trans*-**F8AZO** aggregates reflects from the four local minima of **AZO-FL** linkage induced by the limonene chirality.

## ■ CONCLUSIONS

**AZO**-containing $\pi$-conjugated polymer, poly[(9,9-di-*n*-octylfluorenyl-2,7-diyl)-*alt*-4,4′-azobenzene], (**F8AZO**) has been successfully prepared. The solvent chirality of (*S*)- and (*R*)-limonenes was successfully transferred to **F8AZO**, which allowed for the generation of optically active **F8AZO** aggregates, revealing intense circular dichroism (CD) signals in the visible region. The reversible chiroptical switch was achieved upon alternating photoirradiation at 405 nm (*trans*-form) and 546 nm (*cis*-form). This ability originated from the switching between the *trans*-origin aggregation and *cis*-origin disaggregation of **F8AZO** in the limonene-2-propanol-chloroform tersolvent.

## ■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** Structures, Gaussian03 calculation results (PM3-MM and TD-DFT/B3LYP/3-21G) of **FL-AZO-FL** and **AZO** models, *trans*−*cis* photoisomerization, changes in CD and UV−vis spectra in different poor cosolvents, different ratios of **1*R***/IPA and ratios of **1*S***/**1*R***, and HR−TEM images of *cis*-**F8AZO**. This material is available free of charge via the Internet at http://pubs.acs.org.

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