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Photomodulated Supramolecular Chirality in Achiral Photoresponsive Rodlike Compounds Nanosegregated from the Helical Nanofilaments of Achiral Bent-Core Molecules

Kibeom Kim,[†] Hanim Kim,[‡] Seong-Yong Jo,[†] Fumito Araoka,[§] Dong Ki Yoon,[*,‡] and Suk-Won Choi[*,†]

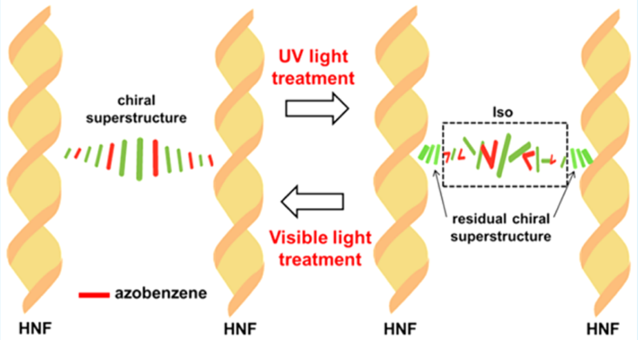
[†]Department of Advance Materials Engineering for Information and Electronics, Kyung Hee University, Yongin-shi, Gyeonggi-do 446-701, Korea

[‡]Graduate School of Nanoscience and Technology and KINC, KAIST, Daejeon 305-701, Korea

[§]Physicochemical Soft Matter Research Unit, RIKEN Center for Emergent Matter Science (CEMS), 2-1 Hirosawa, Wako, Saitama 351-0198, Japan

Supporting Information

ABSTRACT: We prepared a nonchiral mixture of achiral bent-core molecules and photoresponsive rodlike liquid crystalline (LC) molecules. With the help of the isothermal photochemical nematic (N)-isotropic (Iso) phase transition of the photoresponsive rodlike LC molecules, the corresponding phase transition from a dark conglomerate BX phase to another distinguishable dark conglomerate B4 phase took place in the mixture. A large circular dichroism (CD) signal originating from supramolecular chirality was detected in the initial BX phase. On the other hand, the detected CD signal was decreased in the B4 phase after UV irradiation. Interestingly, the decreased CD signal could be reverted to the initial CD signal with visible irradiation. This chiroptical process revealed in this work was stable and reversible and thus opens up the possibility of practical applications such as rewritable optical storage.



KEYWORDS: *chirality, chiroptical switching, liquid crystal, helical nanofilament, circular dichroism, bent-core*

1. INTRODUCTION

Chirality is one of the most attractive subjects in both chemistry and biology.[1] In addition, chirality is an important topic in the field of liquid crystal (LC) science.[2−6] In this study, we explore an intriguing but challenging idea of using the chirality of LC materials to open up the possibility of new practical applications such as rewritable optical storage. The study was motivated by the proposal that achiral or racemic LC phases, in which chirality is induced by the superstructure of LC molecules, might enable the design of new classes of chiroptical materials. Our idea is explored by using bent-core LCs.[7,8] Mesophases found in bent-core molecules are sometimes called "banana phases," as they are specific phases different from conventional phases found in rodlike mesogens. Several banana phases have been chronologically identified and simply designated as B1, B2, B3, etc., where "B" stands for bent, banana, bow, or boomerang.[7] Among them, the helical nanofilament (HNF) B4 phase,[9−12] which is also a class of bent-core phases, is known to segregate into two self-assembling, chiral domains with almost the same probability. Each microscopic chiral domain consisting of HNFs shows high optical rotatory power. In 2005, Takanishi et al. found that the chiral segregated domains become large by mixing achiral rodlike molecules, and a very large chiral conglomerate, B4 phase, formed in a mixed system comprising the bent-core molecule P8−O−PIMB and rodlike molecule 5CB, along with another dark conglomerate, BX phase, that appeared below the B4 phase.[13]

In subsequent studies, it was found that the B4−BX phase transition occurs at nearly the same temperature as the isotropic (Iso)−nematic (N) phase transition of 5CB, which was incorporated into the bent-core molecules.[14] Freeze-fractured transmittance electron microscopy (FFTEM) observations by Zhu et al. suggested that rodlike molecules are nanosegregated from the HNFs of bent-core molecules; the B4 phase in the mixture is formed when the HNFs of the bent-core molecules occur along with rodlike molecules in the Iso phase, whereas the BX phase is formed when the HNFs exist with the rodlike molecules in the N phase.[15] Otani et al. also examined how 5CB molecules behave in the presence of HNFs based on circular dichroism (CD) observations. A relatively small CD signal was observed in the B4 phase of binary mixtures

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comprising bent-core P8−O−PIMB and rodlike 5CB molecules, where 5CB is in the Iso phase. On the other hand, a remarkably enhanced CD signal emerged in the BX phase of the binary nonchiral mixtures, where 5CB is in the N phase.[16] Herein, we prepared a nonchiral mixture of a bent-core molecule and a photoresponsive rodlike LC compound (PRRC). A BX−B4[17] phase transition takes place in the mixture owing to the isothermal photochemical N−Iso phase transition of PRRC, and the observed CD signal can be modulated by irradiation at different wavelengths. This reversible photomodulation of the chiroptical properties can help develop materials for reversible optical storage.

2. RESULTS

2.1. Materials. Several mixtures with different content of bent-core P8−O−PIMB and PRRC were prepared. The PRRC used here was a mixture of 4-butyl-4′-methoxyazobenzene[18,19] (BMAB, 20 wt %) and 5CB (80 wt %). BMAB possesses an azobenzene linkage; the trans form of BMAB stabilizes the N phase of PRRC, whereas its cis isomer tends to destabilize the N phase. As a result, the N−Iso phase transition temperature (T_{NI}) of PRRC with the cis form (T_{NIc}) is much lower than that with the trans form (T_{NIt}).[18] The two isomers of BMAB can be interchanged effectively using light with different wavelengths. The observed T_{NIt} and T_{NIc} of PRRC were 37 and ∼10 °C, respectively. The chemical structures of P8−O−PIMB, BMAB, and 5CB, and the phase diagram of the mixtures consisting of P8−O−PIMB and PRRC are shown in Figure 1.

2.2. Polarized Optical Microscopy (POM) Observations. Typical POM images of the mixture of P8−O−PIMB with 40 wt % PRRC at room temperature (RT, 25 °C) were shown in Figure 2. For POM observations, the mixture was injected into a 2 μm thick quartz cell without any surface treatment such as rubbing. The left column of Figure 2 shows the POM of the mixture before UV irradiation, whereas the right column shows the corresponding images after UV irradiation. The samples were irradiated with UV (microscope lamp; 365 nm, 30 mW cm^{-2}) for 1 min. Dark images were observed under crossed polarizers (Figure 2a), whereas by slightly rotating the upper polarizer clockwise (or anticlockwise) by 10°, two different colored domains were observed (Figure 2b). These two colors were exchanged under the oppositely decrossed condition (Figure 2c). These domains correspond to the previously reported segregated chiral domains with opposite optical rotatory powers.[13] The opposite optical rotatory powers can be easily recognized by rotation of the polarizer (or analyzer) from the crossed polarizers. A color from one domain is exhibited by a clockwise rotation of the polarizer, while from the other domain the color is exhibited by a counterclockwise rotation.[20] This is because the final polarization states in two domains are different when a linearly polarized light passes through two domains with opposite optical rotatory powers.[21] In addition, based on Figure 2 (panels a−c) wherein the brightness of the initial state decreased after UV irradiation, it was suggested that an isothermal phase transition occurred by UV irradiation.

2.3. Grazing Incidence X-ray Diffraction (GIXD) Experiments. The mixtures consisting of P8−O−PIMB and PRRC in the Iso phase (150 °C) were injected between a parallel aligned polyimide (PI)-coated silicon wafer and glass and then cooled to RT. The top glass cover was removed, and the samples were aligned along the direction parallel to the incident X-ray beam. GIXD experiments with a small incident angle (0.13°) were performed using a synchrotron radiation source at the 9A beamline of the Pohang accelerator laboratory (PAL) in South Korea. The size of the focused beam was ∼30 (V) × 290 (H) μm, and the energy was 11.08 keV. The sample-to-detector distance was fixed at 235 mm, and the diffraction patterns were recorded using 2-dimensional (2D) charge-coupled device (CCD, Rayonix SX165). The experimental geometry for the GIXD experiments is illustrated in Figure 3a. As shown in Figure 3 (panels b and c), differences were observed in the GIXD images before and after UV irradiation. The diffraction pattern at $d \sim 4.5$ nm from the HNFs of P8−O−PIMB was consistently observed irrespective of UV irradiation. In contrast, the diffraction pattern at $d \sim 2.2$ nm from PRRC in the small-angle region was distinctively different following UV light irradiation. These results suggest an isothermal N−Iso phase transition, originating from the trans−cis photoisomerization of the azobenzene (BMAB) molecules in PRRC, occurs under UV irradiation.

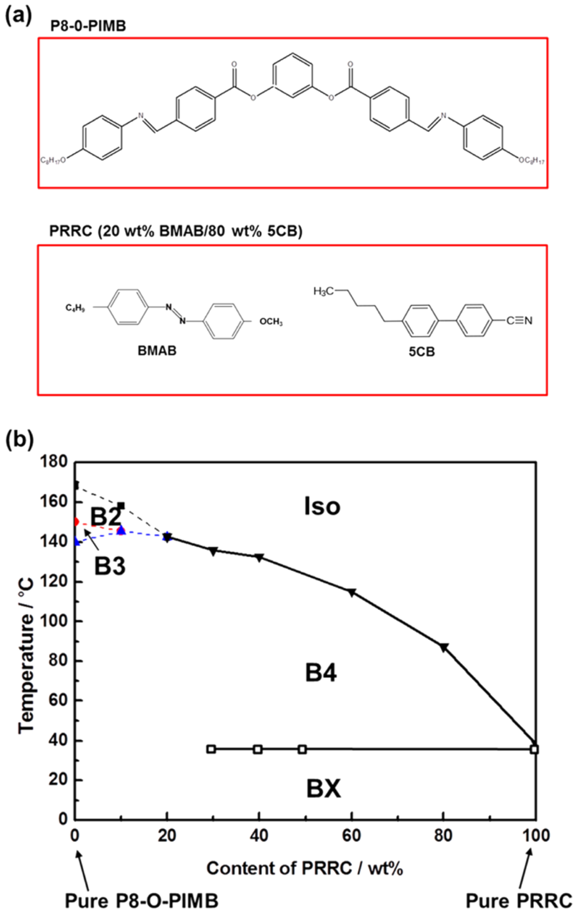

Figure 1. (a) Chemical structures of P8−O−PIMB, BMAB, and 5CB. (b) Phase diagram of the mixtures consisting of P8−O−PIMB and PRRC.

The GIXD results strongly indicate that (1) before UV irradiation, the initial state is a BX phase consisting of a nanosegregated phase formed by the HNFs of P8−O−PIMB surrounded by PRRC in the N phase and (2) after UV irradiation, a B4 phase is formed consisting of a nanosegregated phase formed by the HNFs of P8−O−PIMB surrounded by PRRC in the Iso phase. A BX−B4 phase transition takes place owing to the isothermal photochemical N−Iso phase transition of PRRC. This BX−B4 transition was also suggested by the

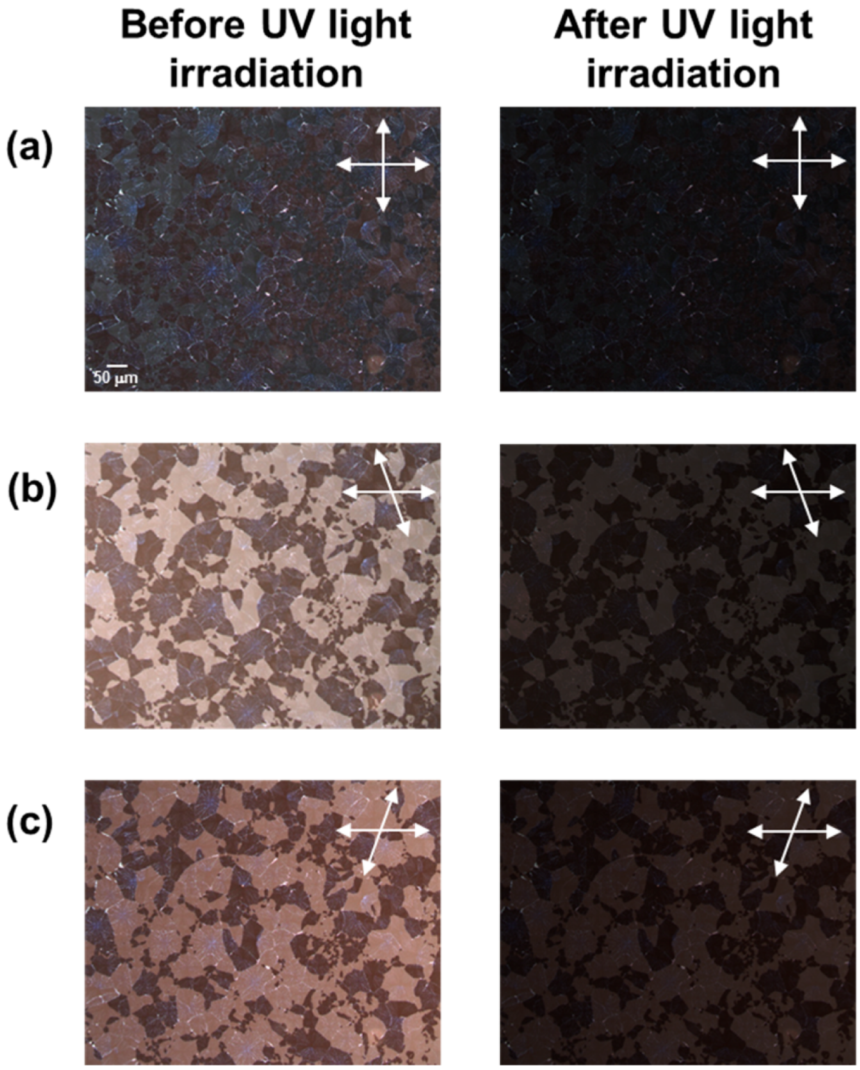

Figure 2. POM images of the mixture of P8−O−PIMB with 40 wt % PRRC at RT (a) under crossed polarizers, (b) slightly decrossed polarizers, and (c) oppositely decrossed polarizers. The arrows indicate the directions of the polarizers. The left column shows POM images before UV irradiation, and the right column shows the corresponding images after UV irradiation.

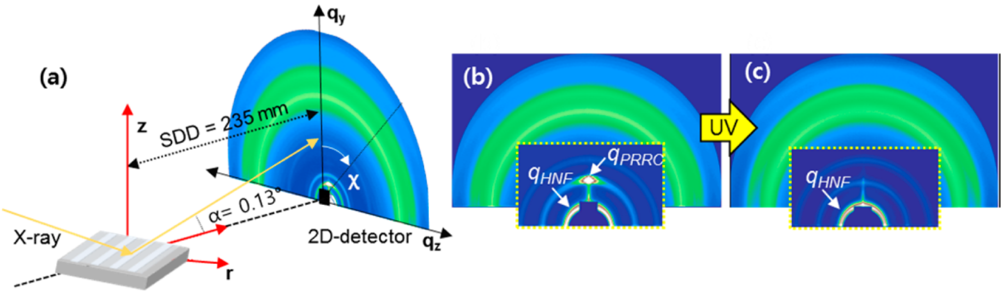

Figure 3. (a) The experimental geometry of GIXD and 2D-GIXD patterns of the mixture of P8−O−PIMB with 40% PRRC (b) before and (c) after UV irradiation.

POM observations, as seen in Figure 2 (panels a−c), wherein the brightness of the initial state decreased after UV irradiation because the birefringence observed in the N phase of PRRC decreased in the Iso phase.

2.4. CD Measurements. We performed CD observations to examine the chirality of the mixtures. The sandwich cells filled with the mixtures consisted of two smooth quartz substrates without surface treatment on either inner surface. The cell-gap of the fabricated cells was 1 μm. The CD spectra were obtained using a specially designed furnace placed in a CD spectrometer (J-720WI, Jasco). To detect the signal from a small domain, focal reducing optics were built up in the optical path of the CD spectrometer. Details on the optical setup for the micromonodomain CD spectrum measurement are described by Araoka et al.[22]

Initially, we did not observe any meaningful CD signals before and after UV irradiation for pure PRRC, which is consistent with the achiral nature of PRRC. Figure 4 shows the

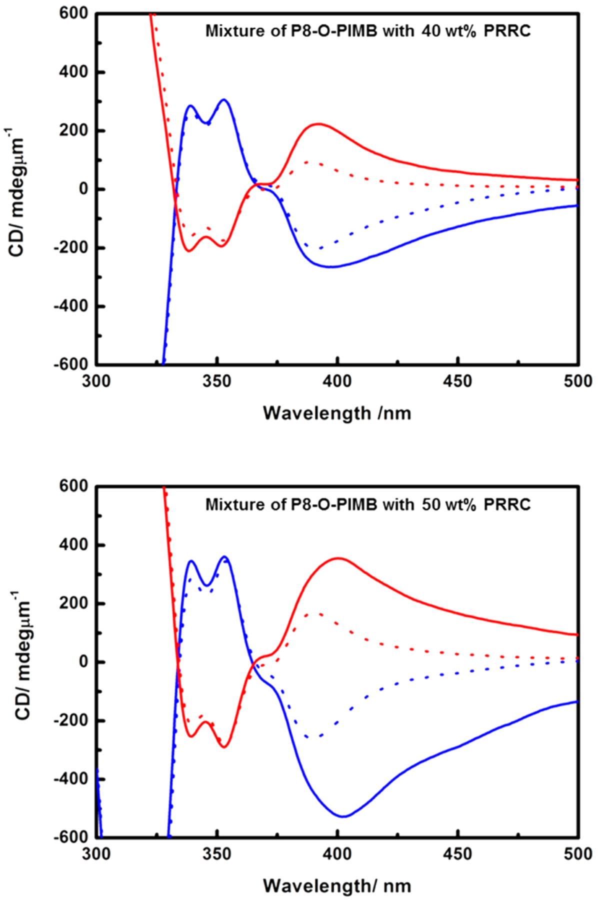

Figure 4. CD spectra of mixtures of P8−O−PIMB and 40 wt % (top) and 50 wt % (bottom) PRRC at RT. The CD spectra in the (+) and (−) domains are shown in red and blue, respectively. The CD spectra before and after UV irradiation are depicted as solid and dotted lines, respectively.

CD spectra of the mixtures of P8−O−PIMB with 40 and 50 wt % PRRC at RT. Very strong CD signals that prevent a quantitative discussion were detected below 330 nm, owing to high absorption of the mixtures, whereas meaningful CD peaks were observed between 330 and 500 nm. Two CD spectra of two chiral domains, which are mirror images, were detected before and after UV irradiation. From the absorption spectra of P8−O−PIMB and the mixture of 60 wt % P8−O−PIMB/40 wt % PRRC, it is noted that the detected induced CD signals originated from PRRC, which was nanosegregated from the HNFs of P8−O−PIMB (Figure S1 in the Supporting Information).

The change in the CD spectra in Figure 4 following UV irradiation indicates that the observed CD intensity critically depends on the phase of PRRC nanosegregated from the HNFs of P8−O−PIMB. The BX phase, in which PRRC in the N phase is nanosegregated from the HNFs, exhibited relatively large CD signals before UV irradiation. On the other hand, the CD signals decreased in the B4 phase, which is a nanosegregated phase formed by the HNFs with PRRC in the Iso phase. Moreover, these CD signal changes were remarkably increased with increasing content of PRRC. Namely, the change in the CD signal following UV irradiation was larger in the mixture containing 50 wt % PRRC than that for those containing 40 wt % PRRC (Figure 4).

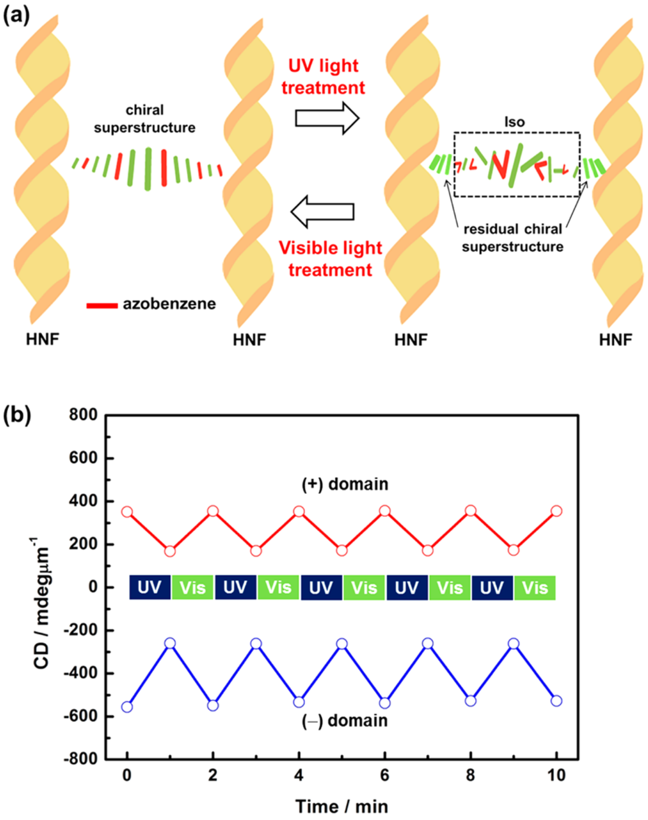

Figure 5. (a) Image showing the mechanism of our phenomenon. (b) Absolute intensity of the CD signal in the mixture containing 50 wt % PRRC at 392 nm for the BX phase and 388 nm for the B4 phase in both (+) and (−) domains as a function of alternating irradiation with UV and visible light at RT.

3. DISCUSSION

Our observations can be explained by Otani's model.[16] An image showing the mechanism of this phenomenon is illustrated in Figure 5a. We consider an initial state (BX), where the N phase of PRRC is located between two right-handed HNFs. If PRRC orients along the groove of the HNFs, PRRC assembles a twisted N-like structure because of the cooperative motion of N LC. This twisted N-like structure is a chiral superstructure, resulting in a CD signal at the absorption band of PRRC. In contrast, by means of UV irradiation, the *cis* isomers of BMAB incorporated into PRRC disturb the N phase. As a result, an isothermal BX−B4 phase transition occurs because of the N−Iso phase transition of PRRC. In the B4 phase, in which the Iso phase of PRRC is located between the HNFs, the assembled chiral superstructures are destroyed, thus decreasing the CD signal. Ideally, the CD signal originating from the supramolecular chirality would completely disappear in the B4 phase; however, a small CD signal remained, as shown in Figure 4. This residual CD signal was detected irrespective of the UV irradiation conditions (light intensity, irradiation time, etc.). This phenomenon can be explained as follows: in the vicinity of the HNFs, the density of LC 5CB molecules in PRRC may be greater than that of the cis isomers of the azobenzene (BMAB) molecules, because the cis isomers tend to move to the bulk regions between the two HNFs.[23,24] Hence, a localized chiral superstructure remains in the vicinity of the HNFs, leading to the detection of a residual CD signal.

Interestingly, the decreased CD signal can be reverted to the initial CD signal with visible irradiation. This is due to cis−trans back-isomerization of the azobenzene molecules incorporated into PRRC. The phase induced by the trans−cis photoisomerization process is reverted to the original phase because the activated cis-isomers reverted to trans-isomers by visible light irradiation. Namely, the Iso phase of PRRC between the two HNFs reverts to the initial N phase under visible irradiation. As shown in Figure 5b, we collected the absolute intensity of the CD signal for the mixture containing 50 wt % PRRC at 392 nm for the BX phase and 388 nm for the B4 phase in both the (+) and (−) domains as a function of alternating irradiation with UV and visible light at RT. The first data point was obtained for the initial BX phase, and the following points were obtained after alternating irradiation with UV (microscope lamp; 365 nm, 30 mW cm^{-2}) and visible light (LED; 450 nm, 80 mW cm^{-2}) for 1 min. In this way, a repeatable absolute CD intensity change was achieved by alternating irradiation at different wavelengths, showing reversible chiroptical modulation.

This reversible chiroptical modulation can be used for rewritable optical storage using irradiation at different wavelengths. For example, the absolute CD intensity is digitized into two states, "0" and "1"; the initial state with large absolute CD intensity is defined as "1," whereas state "0" with small absolute CD intensity is realized after UV irradiation. State "0" can be reverted to the initial state "1" by visible irradiation. Photomodulated BX and B4 in this work were preserved for at least 100 h at RT if there were without unavoidable thermal fluctuations and unintended UV (or visible) light irradiation. Thus, a long-term retention time of "0" and "1" can be anticipated.

4. CONCLUSION

The supramolecular chirality in achiral PRRC nanosegregated from the HNF structures of achiral bent-core molecules could be modulated using a photochemical process. This photomodulated chirality was clearly confirmed using CD observations. In the initial BX phase, a large CD signal at the absorption band of PRRC incorporated into bent-core P8−O−PIMB is due to the chiral superstructure of the N phase of PRRC between the HNFs of P8−O−PIMB. Using UV irradiation, the chiral superstructure can be erased through an isothermal N−Iso phase transition, resulting in a decreased CD signal in the B4 phase. The chiroptical process revealed in this work was stable and reversible, and it thus opens up the possibility of practical applications such as rewritable optical storage.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b07543.

> Absorption spectra of pure P8−O−PIMB and the mixture containing 40 wt % PRRC before and after UV irradiation (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: nandk@kaist.ac.kr.
*E-mail: schoi@khu.ac.kr.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

2D, 2-dimensional
BMAB, 4-butyl-4′-methoxyazobenzene
CCD, charge-coupled device
CD, circular dichroism
FFTEM, freeze-fractured transmittance electron microscopy
GIXD, grazing incidence X-ray diffraction
HNF, helical nanofilament
Iso, isotropic
LC, liquid crystalline
N, nematic
PAL, Pohang accelerator laboratory
PI, polyimide
POM, polarized optical microscopy
PRRC, photoresponsive rodlike LC compound
RT, room temperature
T_{NI}, N−iso phase transition temperature

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