# Reversible Near-Infrared Light Directed Reflection in a Self-Organized Helical Superstructure Loaded with Upconversion Nanoparticles

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**S** *Supporting Information*

**ABSTRACT:** Adding external, dynamic control to self-organized superstructures with desired functionalities is an important leap necessary in leveraging the fascinating molecular systems for applications. Here, the new light-driven chiral molecular switch and upconversion nanoparticles, doped in a liquid crystal media, were able to self-organize into an optically tunable helical superstructure. The resulting nanoparticle impregnated helical superstructure was found to exhibit unprecedented reversible near-infrared (NIR) light-guided tunable behavior only by modulating the excitation power density of a continuous-wave NIR laser (980 nm). Upon irradiation by the NIR laser at the high power density, the reflection wavelength of the photonic superstructure red-shifted, whereas its reverse process occurred upon irradiation by the same laser but with the lower power density. Furthermore, reversible dynamic NIR-light-driven red, green, and blue reflections in a single thin film, achieved only by varying the power density of the NIR light, were for the first time demonstrated.

The ability to tune molecular self-organized superstructures with desired properties using an external stimulus is a major driving force in the bottom-up nanofabrication of intelligent molecular devices. Among the external stimuli such as temperature, electric field, magnetic field, and chemical or electrochemical reaction, light is particularly fascinating owing to its advantage of remote, spatial, and temporal controllability.[1] Light-driven chiral molecular switches or motors in liquid crystal (LC) media capable of self-organizing into optically tunable helical superstructures undoubtedly represent such an elegant example because of their unique property of selective reflection of light and the consequent potential applications.[2] Such systems can be achieved by doping a photoresponsive chiral molecule into a LC host to form a self-organized, optically tunable helical superstructure, that is, a photoresponsive cholesteric LC phase. The resulting macroscopic helical superstructure can reflect light selectively according to Bragg's law and can be tuned by light of an appropriate wavelength. The center wavelength $\lambda$ of the selective reflection is defined by $\lambda = nP$, where $P$ is the pitch length of the helical structure and $n$ is the average refraction index of the LC material. The ability of a chiral dopant to twist an achiral nematic LC phase, that is, helical twisting power (HTP, $\beta$), is expressed in the equation: $\beta = (Pc)^{-1}$ where $c$ is the chiral dopant concentration. The reflection wavelength $\lambda$ can be tuned by the isomerization of photoresponsive dopant molecules upon light irradiation, providing opportunities as well as challenges in fundamental science that open the door for many applications such as tunable color filters,[3] tunable LC lasers,[4] and optically addressed flexible displays without patterned electronics.[5]

It is well established that trans to cis isomerization of azobenzene can be induced by UV light irradiation, whereas its reverse process, cis to trans isomerization, can occur thermally or photochemically with visible light. Recently, the self-organized helical superstructures of cholesteric LCs (CLCs) in a single thin film have been reversibly tuned upon UV or visible-light irradiation by doping chiral azobenzene with a high HTP value into a LC host.[6] Unfortunately, the use of high-energy UV light might result in material decomposition, poor penetration through the substrate, and so forth. Although extensive efforts have been made to design chiral azobenzene switches that can be triggered with longer wavelengths of light, that is, visible or even near-infrared (NIR) light, so far there are only very few reports on reversible visible light tuning in LC.[7] To the best of our knowledge, reversible or irreversible NIR-light guided tuning of self-organized helical superstructures has not yet been realized to date. Use of NIR light would be much more desirable than either UV or visible light in the fields such as life science, materials science, and aerospace because of its superior penetration and invisibility for remote activation of materials at a specific time and location with relatively low interference and high precision. Therefore, it is of paramount importance to develop NIR responsive photonic materials with functionalities. Recently, upconversion nanoparticles (UCNPs) are attracting much attention especially in biomedical applications owing to their promising and advantageous ability to efficiently convert NIR light to UV/visible lights.[8] UCNPs have been used for sensitizing and activating photoresponsive systems where UV or visible light are not suitable. Although

UCNPs have been used in the study of polymeric systems[9] mostly for drug delivery, there has been no report on the use of UCNPs in a CLC to tune the self-organized helical superstructures.

Herein, we report that a novel self-organized helical superstructure, fabricated by doping the new light-driven chiral molecular switch **4** and UCNPs in a LC composed of commercially available components, was found to exhibit unprecedented reversible NIR-light guided tunable behaviors only by modulating the excitation power density of continuous-wave NIR laser (980 nm) (Figures 1 and 2). This reversible
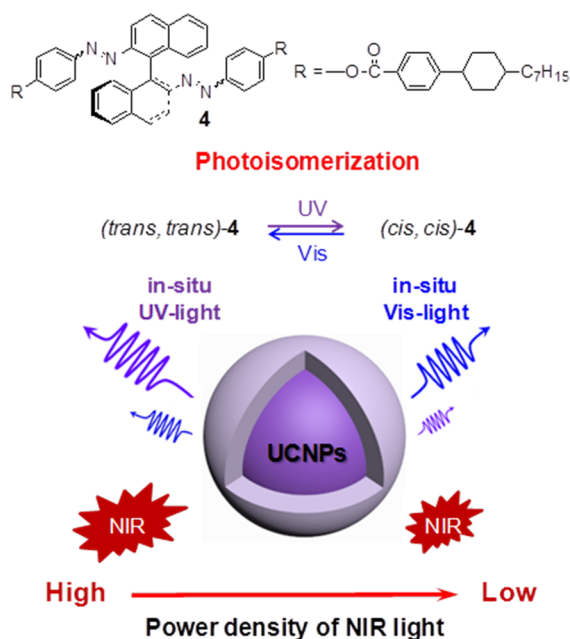


**Figure 1.** Molecular structure of light-driven chiral switch **4** and schematic description of the photoisomerization of this chiral azobenzene **4**, which is triggered in a remote control process using the in situ UV light generated under the NIR light with a high excitation power density and the in situ visible light generated under the same wavelength NIR light but with low excitation power density when the UCNPs are irradiated by 980 nm NIR laser.
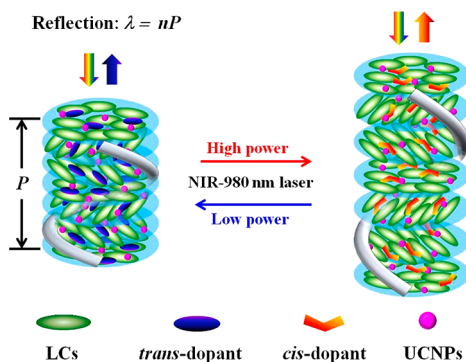


**Figure 2.** Schematic mechanism of reversibly tuning of self-organized helical superstructures with chiral switch **4** and UCNPs upon irradiation of NIR laser at different power densities.

tuning process results from the fact that chiral switch **4** exhibits reversible photoisomerization when absorbing the UV or visible upconversion emissions from UCNPs and the intensity ratio of the emissions at different wavelengths is highly dependent on

the excitation power density of the 980 nm NIR laser. At the high power density, the ultraviolet emissions are prominent and decisive to drive the trans to cis isomerization of **4**, whereas the visible light generated from the same UCNPs at the low power density triggers the reverse cis to trans photoisomerization. In other words, the chiral switch **4** exhibits reversible trans to cis and cis to trans photoisomerization cycles, both induced only by modulating the excitation power density of 980 nm NIR light. Furthermore, reversible dynamic NIR-light-driven red, green, and blue reflections in a single thin film were for the first time demonstrated only by varying the power density of the NIR light.

The new chiral switch **4** was prepared by a facile synthesis, and its chemical structure was well identified by ^{1}H and ^{13}C NMR spectroscopy, high-resolution mass spectrometry, and elemental analysis (see Supporting Information). Chiral switch **4** exhibited superior solubility in LC host and high HTP values and considerable differences in HTP among their various states. For example, its HTP value in LC E7 decreased from 105.7 to 60.5 $\mu m^{-1}$ upon photoisomerization from the initial state to the photostationary state (Supporting Information Figure S4). For UCNP, its synthesis is straightforward (see Supporting Information).[10] However, to achieve a high efficiency of upconversion emission from NIR to UV, the novel $\beta$-NaGdF$_4$: 70 mol % Yb$^{3+}$, 1 mol % Tm$^{3+}$ @ $\beta$-NaGdF$_4$ core−shell nanostructures were synthesized according to our previously reported procedure[11] and characterized by transmission electron microscopy (TEM) and power X-ray diffraction (XRD) analysis. The TEM image of the as-prepared core−shell UCNPs clearly shows size and shape uniformity with an average diameter of ∼72 nm (Figure 3A). From the
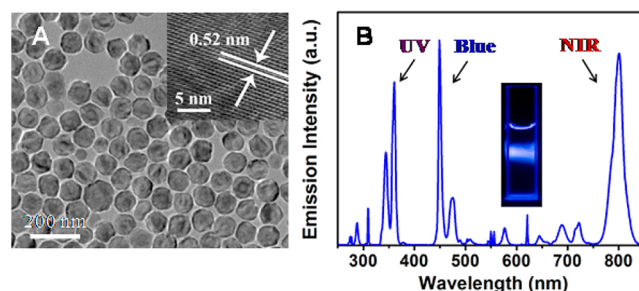


**Figure 3.** (A) TEM and high resolution TEM (the inset) images of $\beta$-NaGdF$_4$: 70 mol %Yb$^{3+}$, 1 mol %Tm$^{3+}$ @ $\beta$-NaGdF$_4$ core−shell UCNPs; (B) upconverting emission spectrum of the UCNPs (60 $\mu g$/mL) in cyclohexane at room temperature upon irradiation by 980 nm NIR laser (1 W/mm$^2$), the inset shows the photograph of upconversion luminescence from the UCNPs in cyclohexane.

powder XRD pattern (Supporting Information Figure S9), it can be seen that the nanocrystals display a hexagonal phase of NaGdF$_4$, which was further confirmed by the observation of the lattice distances of 0.52 nm in the high-resolution TEM image (the inset in Figure 3A). Figure 3B illustrates the upconverting emission spectrum of the UCNPs (60 $\mu g$/mL) in cyclohexane at room temperature upon irradiation by 980 nm NIR laser (1 W/mm$^2$), the emission peaks mainly located at 290, 343, 365, 450, 475, and 800 nm corresponding to the $^1I_6-^3H_6$, $^1I_6-^3F_4$, $^1D_2-^3H_6$, $^1D_2-^3F_4$, $^1G_4-^3H_6$, and $^3H_4-^3H_6$ upconverting transitions, respectively (Supporting Information Figure S10).

It is worth noting here that the intensity ratio of upconverting emissions in different wavelength regimes is largely dependent on the excitation power density of the 980

nm NIR laser (Supporting Information Figure S11 and S12). For example, the ultraviolet upconverting emission from the UCNPs are greatly increased at high power density (2 W/mm$^2$), whereas the visible emission dominates the spectrum at low power density (0.15 W/mm$^2$) as shown in Figure 4. As is
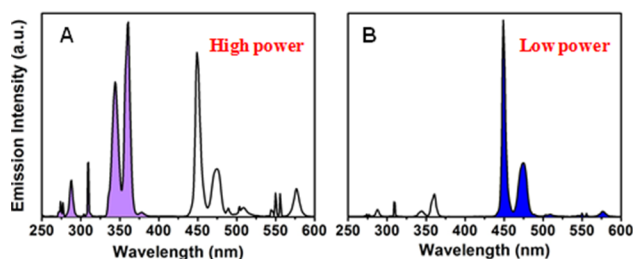


**Figure 4.** Emission spectra of UCNPs (60 $\mu$g/mL) in cyclohexane at room temperature upon irradiation with 980 nm NIR laser (A) at high power density (2 W/mm$^2$) and (B) at low power density (0.15 W/mm$^2$).

known, visible emissions generated from $^1G_4-^3H_6$ (475 nm) and $^1D_2-^3F_4$ (450 nm) transitions are three- and four-photon processes, respectively, whereas the ultraviolet emissions derived from $^1D_2-^3H_6$ (365 nm), $^1I_6-^3F_4$ (343 nm) and $^1I_6-^3H_6$ (290 nm) involve four- and five-photon processes. Thus, higher excitation power density is needed to achieve a UV-emission-dominated spectral profile by first saturating other visible and NIR transitions.[12] Importantly, the main upconversion emission peaks of the UCNPs in the UV regions of the spectrum (290−400 nm) at high power density have appropriate spectral overlap with the $\pi \rightarrow \pi^*$ absorption bands of (*trans, trans*)-**4** in cyclohexane solutions, making it possible for the emitted UV light of UCNPs to trigger its trans to cis isomerization. On the other hand, the visible upconversion emissions (450−550 nm) at low power density have suitable spectral overlap with the n$\rightarrow \pi^*$ absorption bands corresponding to *cis*-azobenzene, which can in turn be utilized to drive the reverse cis to trans isomerization (Supporting Information Figure S14).

Figure 5 illustrates the changes in the UV−vis spectra of chiral switch **4** (60 $\mu$g/mL) and UCNPs (2 mg/mL) in cyclohexane at room temperature upon irradiation with 980 nm NIR laser. The dark incubation of the solution served to maximize the absorption at 365 nm corresponding to the initial state, that is, (*trans, trans*)-**4**. When irradiated by 980 nm NIR laser at high power density, the solution showed the
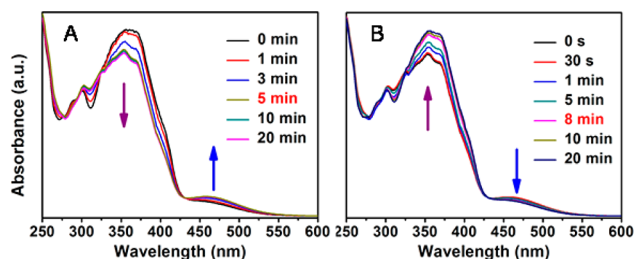


**Figure 5.** Changes in the UV−vis spectra of chiral switch **4** (60 $\mu$g/mL) and UCNPs (2 mg/mL) in cyclohexane at room temperature in going from (A) the initial state to PSS$_{980H}$ upon irradiation with 980 nm NIR laser at high power density (2 W/mm$^2$) and (B) from PSS$_{980H}$ to PSS$_{980L}$ upon irradiation with 980 nm NIR laser at low power density (0.15 W/mm$^2$).

isomerization to a photostationary state (PSS$_{980H}$), as evidenced by a decrease in the absorbance at about 365 nm (Figure 5A). The PSS$_{980H}$ for conversion of (*trans, trans*)-**4** toward (*cis, cis*)-**4** was reached within approximately 5 min at room temperature. The reverse process was achieved within approximately 8 min upon irradiation with 980 nm NIR laser at low power density as shown in Figure 5B. The distinct changes gave clear evidence that the chiroptical properties of **4** can be modulated by NIR 980 nm laser, and the reversible trans to cis and cis to trans photoisomerization process can be induced only by modulating the excitation power density of the 980 nm laser. In addition, the upconversion luminescence intensity of the UCNPs decreased significantly with an increase in the concentration of **4**, which also indicates that the upconversion emission can be effectively quenched by chiral switch **4** through the emission−reabsorption process and intermolecular energy transfer from the UCNPs to **4** (Supporting Information Figure S13).[13]

To tune the self-organized helical superstructures of CLCs and their dynamic reflection colors, both the UCNPs and chiral switch **4** were doped into a LC media. The resulting mixture was capillary-filled into a 10 $\mu$m thick planar aligned cell with antiparallel rubbing direction. The shift in the photonic band gaps upon NIR light irradiation was recorded using a spectrometer incorporated into the polarizing optical microscope. Interestingly, 3 wt % chiral switch **4** and 1.5 wt % UCNPs in commercially available 80.5 wt % nematic LC E7 and 15 wt % S811 were found to exhibit reversibly tunable NIR-light-directed reflections through red, green, and blue wavelengths only by varying the power density of the excitation NIR light (Figure 6). The center reflection wavelength was
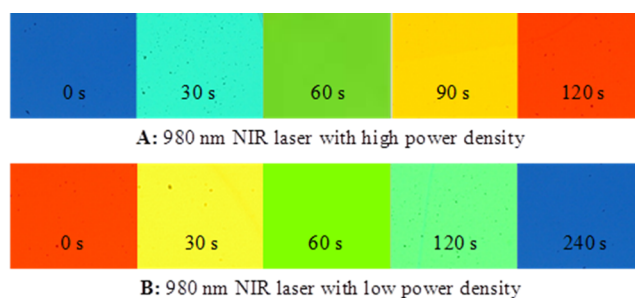


**Figure 6.** Reflection colors of the CLCs with 3 wt % chiral molecular switch **4** and 1.5 wt % UCNPs in a 10 $\mu$m thick planar cell at room temperature, taken from a polarized reflective mode microscope (A) upon irradiation with 980 nm NIR laser at high power density (2 W/mm$^2$) and followed by (B) irradiation with 980 nm NIR laser at low power density (0.15 W/mm$^2$).

around 435 nm at the initial state (Figure 7). Upon irradiation with 980 nm NIR laser at high power density, the reflection wavelength was tuned to 540 nm in 60 s and further reached a photostationary state in 120 s with a center reflection wavelength at 625 nm. The reverse process across red, green, and blue reflection colors occurred within approximately 4 min upon irradiation with 980 nm NIR laser at low power density (Figure 7). The reversible tuning of reflection across red, green, and blue reflection colors was repeated many times without noticeable degradation.

In conclusion, a NIR-light-responsive self-organized helical superstructure was fabricated by doping the new light-driven chiral switch and the UCNPs with high upconversion efficiency into a LC host composed of commercially available components. More interestingly, the resulting photoresponsive
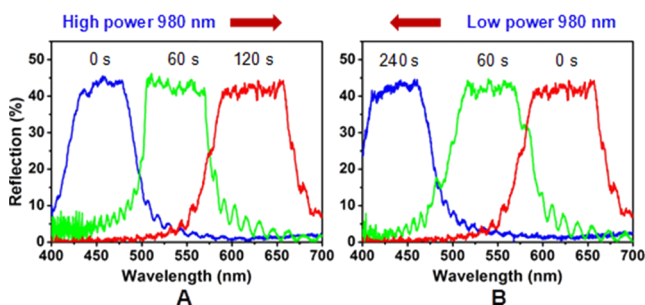
**Figure 7.** Corresponding reflection spectra of above CLC at room temperature (A) upon irradiation with 980 nm NIR laser at high power density (2 W/mm$^2$) for different times and (B) upon irradiation with 980 nm NIR laser at low power density (0.15 W/mm$^2$) for different times.

helical superstructures can be reversibly tuned simply by modulating the excitation power density of the 980 nm NIR laser. Furthermore, reversible dynamic NIR-light-driven red, green, and blue reflections in a single thin film, achieved only by varying the power density of the NIR light, were for the first time demonstrated. The concept disclosed and demonstrated here offers a convenient and versatile method to spatially and temporally regulate the self-organized helical photonic super-structures and their dynamic reflections. This study also shows that synergetic effects of appropriate materials combinations can yield functional materials with applicable properties.

## ■ ASSOCIATED CONTENT

**ⓢ Supporting Information**
Materials and methods, synthetic procedures, and characterizations. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**
The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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