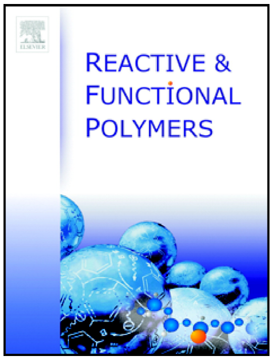

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Abstract

Cholesteric liquid crystal (CLC) exhibits selective reflection, making it a great application in the field of light control. Here, a near-infrared light (NIR) was used to drive the self-organizing spiral superstructure of the cholesteric liquid crystal to adjust the reflection notch. The polymer dye **M2** with near-infrared absorption properties was synthesized by thiol-ene click polymerization and [2 + 2] click reaction; and has good solubility in the CLC system. **M2** absorbs near-infrared light to increase the temperature of the system and the temperature-sensitive chiral dopant CD can realize the photothermal tuning of CLC system by the spiral twisting force of CLC with the change of temperature. The use of near-infrared light is beneficial compared to ultraviolet (UV) and visible light because of its invisibility, high penetration and ease of remote control. The entire CLC system has good near-infrared absorption, fast light response and a wide adjustable range.

Keywords: Cholesteric liquid crystal; Near-infrared light; Click reaction; Photothermal tuning.

thermal tuning of cholesteric liquid crystal

1. Introduction

Responsive materials have attracted much attention for their great application value. In general, the reflected light of responsive materials is based on periodic structures rather than dyes that is the basic strategy for most organisms to transmit optical signals in nature.[1] When a creature is exposed to external stimuli, it will voluntarily produce a change in color. Scientists have designed many responsive materials through similar principles. They can not only obtain a variety of color changes but also can be adjusted in a variety of ways, such as light,[2-4] heat,[5] electricity,[6, 7] stress and so on.[8]

Cholesterol liquid crystals (CLCs) - also known as chiral nematic liquid crystals (N*-LC) have a spontaneous self-assembling periodic helical superstructure.[9, 10] The spiral superstructure of CLC is characterized by two structural parameters: the handedness and the pitch. The direction in which the director rotates about the helical axis defines its direction of rotation, while the pitch length (p) corresponds to the distance over which the director rotates a full turn.[11] It is well known that the orientation of CLC molecules changes in a spiral manner, so that light is selectively reflected according to Bragg's law.[12] The selective reflection is determined by the pitch of the helix in the CLC and can be adjusted due to the dynamic control of the self-organizing helical superstructure by external stimuli. CLC's selective reflection has many applications, such as tunable lasers,[13-15] optical switches[16, 17] and information storage. However, in a variety of easily available stimuli, light has many advantages such as remote, local, spatial and temporal controllability, rapid response and so on.

Currently, the tuning methods of photothermal and electrothermal effects have attracted more and more attention. Wang et al designed a self-organized helical superstructure impregnated with unique mesogen- modified gold nanorods. The inertial inversion was shown when the NIR was irradiated, resulting from the significant photothermal effect of the embedded gold nanorods.[18] Wu et al proposed a new method based on the electrothermal effect. By applying an AC voltage, the reflection color can be adjusted in a wide wavelength range to cover the entire visible spectrum.[19] Hsiao et al prepared an organic membrane with a self-organized spiral superstructure. The organic film is a dual-frequency thermosensitive cholesterol (DFTC) material, which is composed of a liquid crystal body doped with a binary chiral dopant mixture including a thermal chiral switch. The red, green and blue reflections in the DFTC film can be obtained by causing the dielectric to heat by changing the frequency of the applied voltage of 45 V_{rms}.[20] Based on the above-mentioned literature investigation, we doped polymer near-infrared dye into the CLC system for the first time and used NIR light to regulate the spiral structure of CLC. The most common means of photoresponsive CLC preparation is to add a small amount of photochromic chiral molecular switches, such as azobenzenes, dialkylethylenes, etc. to the nematic LC host.[21, 22] However, such systems generally require ultraviolet (UV) or visible light stimulation. High-energy ultraviolet rays are harmful to the human body and have poor penetrability that easily leads to material aging and environmental pollution. Compared with ultraviolet/visible light, near-infrared light has the advantages of invisibility and strong penetrating power, and can remotely control the spiral upper layer structure. It has great application value in special fields such as life science, aerospace and other fields.

Therefore, a polysiloxane side chain liquid crystal polymer dye **M2** was synthesized with near-infrared absorption properties by thiol-ene click polymerization and [2 + 2] click chemistry.[23-26] Two side chains with different functions are branched onto the flexible main chain PMMS (Poly[3mercaptopropylmethyl-siloxane]), one is the liquid crystal monomer AC-6CN, and the other is an aniline derivative having a clickable triple bond. The presence of AC-6CN allows **M2** to have better solubility in the CLC system, while the aniline derivative after F_4-TCNQ click has strong absorption characteristics in the near-infrared region. **M2** was added to the CLC system and equipped with a chiral dopant CD with temperature-sensitive properties. Under NIR light stimulation, the entire CLC has good absorption, fast responsiveness and a wide tunable wavelength range.

2. Experimental

2.1 Materials and instrumentations

2.1.1 Materials

Poly[3-mercaptopropylmethyl-siloxane] (PMMS, SMS-992, M.W. 4000-7000, 95 cst) was purchased from Gelest Inc. 2,2-Dimethoxy-2-phenylacetophenone (DMPA) and copper (I) iodide were purchased from Aladdin Inc. 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoqui-nodimethane (F_4-TCNQ), 4-iodophenol, 4-iodoaniline, 1-bromobutane and 3-bromoprop-1-ene were purchased from Energy Chemical. Trans-Dichlorobis (triphenyl-phosphine) Palladium (II) and Trimethylsilylacetylene (TMSA) were purchased form Sinopharm. Potassium iodide, Anhydrous acetonitrile, Anhydrous methanol (MeOH) and Potassium carbonate were purchased from Beijing Dominant Technology Co. These chemicals were of commercially analytical grade. Dichloromethane (DCM), triethylamine (TEA) and N, N-Dimethylformamide (DMF) were distilled on CaH_2 under nitrogen. Tetrahydrofuran (THF) was distilled on sodium benzophenone ketyl undernitrogen. Other chemical reagents were used without further purification.

thermal tuning of cholesteric liquid crystal

LC, (SLC-1717, n_o = 1.519, n_e = 1.720, n = n_e - n_o = 0.201, T_{N-I} = 92°C) was purchased from Shijiazhuang Yongsheng Huatsing Liquid Crystal Co. Ltd. 6-((4'-cyano-[1,1'-biphenyl]-4-yl)oxy)hexyl acrylate (AC-6CN) as liquid crystal side chain for **M1** was purchased from Shijiazhuang Yongsheng Huatsing Liquid Crystal Co. Ltd. (+)[1,1'-binaphthalene]-2,2'-diyl bis(4'-(2-methylbutyl)-[1,1'-biphenyl]-4-carboxylate) as a chiral dopant, it was synthesized in our previous work.[27] The molecular formulas of chiral dopant and side chain liquid crystal monomers are shown in Figure 1.

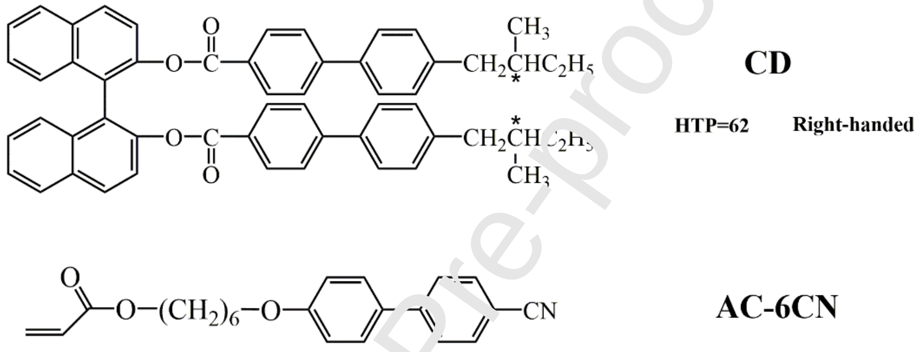


Figure 1. Chemical structure of chiral dopant CD and AC-6CN.

2.1.2 Instrumentations

All ^{1}H-NMR spectra were obtained using BRAKER AVANCE III HD NMR spectrometer (500 MHz) at 25°C using deuterated chloroform ($CDCl_3$) with tetramethylsilane (TMS) as the internal standard. The FT-IR spectra were collected using a Perkin Elmer LR-64912C Fourier transform infrared spectrometer. Thermogravimetric analysis (TGA) was performed on a TAQ600 at a heating rate of 10°C · min^{-1} under nitrogen. Gel permeation chromatography (GPC) was performed on an HP 1100 high pressure liquid chromatography (HPLC), equipped with an HP 1047A refractive index detector and a Plgel MIXED-C 300-7.5 mm column (packed with 5 µm particles). The column packing allowed the separation of polymers over a wide molecular weights (200-3000000g/mol). THF was used as the eluent at a low flow rate of 1 mL·min^{-1} at 35°C Polystyrene standards were used as the references. All MALDI-TOF-MS spectra were recorded on a Shimadzu AXIMA-CFR mass spectrometer. The operation was performed at an accelerating potential of 20 kV in a linear positive ion mode with dithranol as a matrix. Elemental analyses were performed at the Institute of Chemistry, Chinese Academy of Sciences, with a Flash EA 1112 instrument. The reflection spectra and UV absorption were recorded in a quartz cuvette using a JASCO V-570 spectrophotometer. Polarized optical microscopy (POM) was carried out to observe the liquid crystal textures of the samples using a Carl Zeiss Axio Vision SE64 polarized optical microscope with a Linkam LTS420 hot stage. ST9450 handheld thermal imager collects thermal imaging images. Power-adjustable BD-808 near-infrared laser as light-tuned light source. Power-adjustable FUV-6BK UV curing device for inducing UV polymerization.

2.1.3 cell conditions

Two types of liquid crystal cells have been prepared. As shown in Figure 2.(One was a glass liquid crystal cell. Figure 7 (b) (c) was given after measurement using a glass liquid crystal cell. Another type used a flexible PET cell, and Figure. 7 (a) and Figure 8 used a PET cell) The preparation process of the LCD cell is as follows: Preparation process of the liquid crystal cell: the glass containing the ITO layer was cut into a size of 1 cm * 1.5 cm, cleaned and oriented. PET (polyethylene terephthalate) film (10 μm thick) is used as cell spacers. The two pieces of glass were glued together through spacers to prepare a liquid crystal cell. The LC, **M2** and CD system was mixed uniformly and filled into the cells by capillary action. Preparation of flexible PET liquid

thermal tuning of cholesteric liquid crystal

crystal cell: The transparent PET film (5 µm thick) was cut to a size of 1 cm * 1 cm and cleaned. Add a small amount of the mixed LC system to the PET film and squeeze it with another PET film to spread the liquid crystal uniformly.

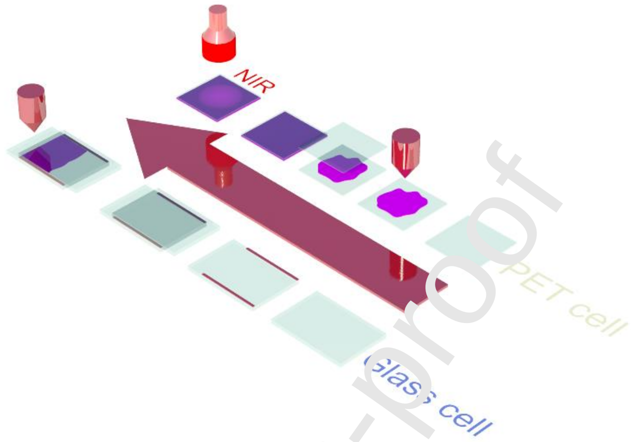


Figure 2 Preparation process of glass liquid crystal cell and PET cell

2.2 Synthetic procedures

2.2.1 1-(allyloxy)-4-iodobenzene (1)

3-bromoprop-1-ene (1.21 g, 0.01 mol), 4-iodophenol (2.2 g, 0.01 mol) and anhydrous potassium carbonate (1.38 g, 0.01 mol) were added in anhydrous acetonitrile (100 mL). The mixture was stirred at 85°C for 3 h, filtration to remove inorganic salts, evaporation and column chromatography (SiO_2, $V_{petroleum\ ether\ (PE)}/V_{dichloromethane(DCM)}$ = 2:1) accorded the desired product **1** as a colorless oily liquid with a yield of 96%. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 5.57 (d, J = 9.0 Hz, 2H), 6.72 (d, J = 9.0 Hz, 2H), 6.00-6.10 (m, 1H), 5.43 (d, J = 17.5, 1H), 5.32 (d, J = 10.5 Hz, 1H), 4.53 (d, J = 5.5 Hz, 2H) ppm. FT-IR (KBr, cm^{-1}): ν = 3083, 2865, 1586, 1487, 1286, 1245, 993, 812, 583, 501. MALDI-TOF-MS (dithranol): m/z: calcd for C_9H_9IO: 259.97 g · mol^{-1}, found: 261.3 g · mol^{-1}

$[MH]^+$; elemental analysis calcd (%) for C_9H_9IO (259.97): C 41.56, H 3.49, O 6.16, found: C 41.56, H 3.50, O 6.17.

2.2.2 polymer (2)

Compound **1** (110 mg, 0.42 mmol), PMMS (275.2 mg, 2 mmol -SH), DMPA (20 mg 2 wt%) and 15 mL THF were added into a dry 20 mL glass vessel. The vessel was radiated under a 50 W UV light (λ_{max} = 365 nm) for 30 min with mild agitation. Then AC-6CN (570 mg, 1.62 mmol) was added in the same glass vessel and continue to irradiate for 30 min. The solution was poured into a large excess amount of methanol. The precipitate was collected by filtration, washed with methanol and dried under vacuum. The desired product **2** was a colorless viscous liquid, obtained via thiol-ene click reaction in 85% yield. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 7.78-7.45 (m, 2.22H), 7.08-6.91 (m, 0.76H), 6.74-6.60 (m, 0.20H), 4.30-3.90 (m, 1.73H), 2.91-2.45 (m, 2.04H), 2.09-1.99 (m, 0.22H), 1.92-1.41 (m, 4.76H), 0.76-0.53 (m, 1H), 0.22-0.04 (s, 1.5H) ppm. FT-IR (KBr, cm^{-1}): ν = 3065, 2920, 1879, 1586, 1488, 1241, 1175, 1079, 792, 508, 434.

2.2.3 N, N-dibutyl-4-iodoaniline (3)

To a degassed solution of 4-iodoaniline (4.38 g, 0.02 mol), 1-bromobutane (8.65 g, 0.05 mol) in N, N-Dimethylformamide (DMF) (100 mL), anhydrous potassium carbonate (1.38 g, 0.01 mol) and potassium iodide (1.66 g, 0.01 mol) were added under Ar. The mixture was refluxed under magnetic stirring at 120°C for 20 h. After removal of the precipitated salt, the organic phase was washed three times with water, drying over Na_2SO_4, the solution was filtered. Removal of the solvent in vacuo and purification on column chromatography (SiO_2, V_{PE}/V_{DCM} = 3:1) afforded 70% yield of the desired product **3** as a Colorless oily liquid. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 7.44 (d, J = 9.0

Hz, 1H), 6.44 (d, J = 9.0 Hz, 1H), 3.25 (t, J = 7.5 Hz 2H), 1.53-1.61(m, 2H), 1.30-1.42 (m, 2H), 0.98 (t, J = 7.5 Hz, 3H) ppm. FT-IR (KBr, cm^{-1}): ν = 3085, 2958, 2864, 1744, 1588, 1469, 1392, 1287, 1184, 1100, 986, 906, 804, 697, 434. MALDI-TOF-MS (dithranol): m/z: calcd for $C_{14}H_{22}NI$: 331.08 g · mol^{-1}, found: 332.05 g · mol^{-1} [MH]$^+$; elemental analysis calcd (%) for $C_{14}H_{22}NI$ (331.08): C 50.76, H 6.69, N 4.23, found: C 50.77, H 6.70, N 4.23.

2.2.4 N, N-dibutyl-4-((trimethylsilyl) ethynyl) aniline (4)

To a degassed solution of **3** (332 mg, 1.00 mmol) and trimethylsilylacetylene (TMSA) (147 mg, 1.50 mol) in triethylamine (TEA) (30 mL) and tetrahydrofuran (THF) (30 mL), bis (triphenylphosphine) palladium (II) dichloride ($PdCl_2(PPh_3)_2$) (70.2 mg, 0.10 mmol) and cuprous iodide (CuI) (20 mg, 0.10 mmol) were added under Argon. The mixture was refluxed under magnetic stirring at 40°C for 8 h. After removal of the catalyst, solvent evaporation and purification on column chromatography (SiO_2, V_{PE}/V_{DCM} = 6:1) afforded 83% yield of the desired product **4** as a yellow oily liquid. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 7.32 (d, J = 9.0 Hz, 1H), 6.54 (d, J = 9.0 Hz, 1H), 3.29 (t, J = 8.0 Hz, 2H), 1.63-1.53 (m, 2H), 1.32-1.42 (m, 2H), 0.98 (t, J = 7.0 Hz, 3H), 0.26(s, 4.5H)ppm. FT-IR (KBr, cm^{-1}): ν = 3098, 2953, 2897, 2148, 1874, 1609, 1515, 1462, 1368, 1245, 869, 757, 535. MALDI-TOF-MS (dithranol): m/z: calcd for $C_{19}H_{31}NSi$: 301.22 g · mol^{-1}, found: 302.3 g · mol^{-1} [MH]$^+$; elemental analysis calcd (%) for $C_{19}H_{31}NSi$ (301.22): C 75.68, H 10.36, N 4.65, found: C 75.69, H 10.37, N 4.65.

2.2.5 N, N-dibutyl-4-ethynylaniline (5)

Compound **4** (1.508 g, 0.005 mol) and anhydrous potassium carbonate (692 mg, 0.005 mol) were dissolved in THF/MeOH (V_{THF}/V_{MeOH} = 7:3, 100 mL). The mixture was refluxed under magnetic stirring at room temperature for 3 h; the inorganic salts were then removed and evaporated. The organic layer was purified using a silica gel column (SiO_2, DCM) obtaining a yellow-green oily product **5** with a yield of 98%. ^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 7.35 (d, J = 9.0 Hz, 1H), 6.56 (d, J = 9.0 Hz, 1H), 3.29 (t, J = 7.5 Hz, 2H), 2.98 (s, 0.5H), 1.64-1.53 (m, 2H), 1.33-1.42 (m, 4H), 0.98 (t, J = 7.5 Hz, 3H) ppm. FT-IR (KBr, cm^{-1}): ν = 3304, 3093, 2956, 2098, 1740, 1607, 1367, 1148, 1007, 928, 814, 740, 529. MALDI-TOF-MS (dithranol): m/z: calcd for $C_{16}H_{23}N$: 229.18 g · mol^{-1}, found: 230.2 g · mol^{-1} $[MH]^+$; elemental analysis calcd (%) for $C_{16}H_{23}N$ (229.18): C 83.79, H 10.11, N 6.10, found: C 83.79, H 10.12, N 6.09.

2.2.6 polymers (M1)

Compound **2** (300 mg) and **5** (41.5 mg, 0.18 mmol) were dissolved in THF/TEA (V_{THF} /V_{TEA} = 1:1, 20 mL). After the solution was degassed under nitrogen for 30 min, then added $PdCl_2(PPh_3)_2$ (120 mg, 0.17 mmol) and CuI (21 mg, 0.11 mmol). The reaction mixture was stirred at 40°C for 3 h under Ar. The mixture was filtered to remove the catalyst and mixed with a large excess amount of methanol. The precipitate was collected by filtration. After washing with methanol and drying under vacuum, a yellow gelatinous solid polymer **M1** was obtained in a yield of 81%. FT-IR (KBr, cm^{-1}): ν = 2918, 2848, 2223, 2134, 1732, 1642, 1601, 1491, 1382, 1246, 1175, 1072, 819, 533.

2.2.7 polymers (M2)

M1 (150 mg) and F_4-TCNQ (27.9 mg, 0.10 mmol) were dissolved in 1,2-dichloroethane (DCM) (4 mL) under Argon. The mixture was stirred for 3 h at 25°C and then the solution was poured into a large excess amount of methanol. The precipitate was collected by filtration, washed with MeOH and dried under vacuum. The desired product **M2** was a green solid with a yield of 91%. FT-IR (KBr, cm^{-1}): ν = 2935, 2863, 2196, 1733, 1604, 1493, 1397, 1250, 1177, 1073, 822, 534.

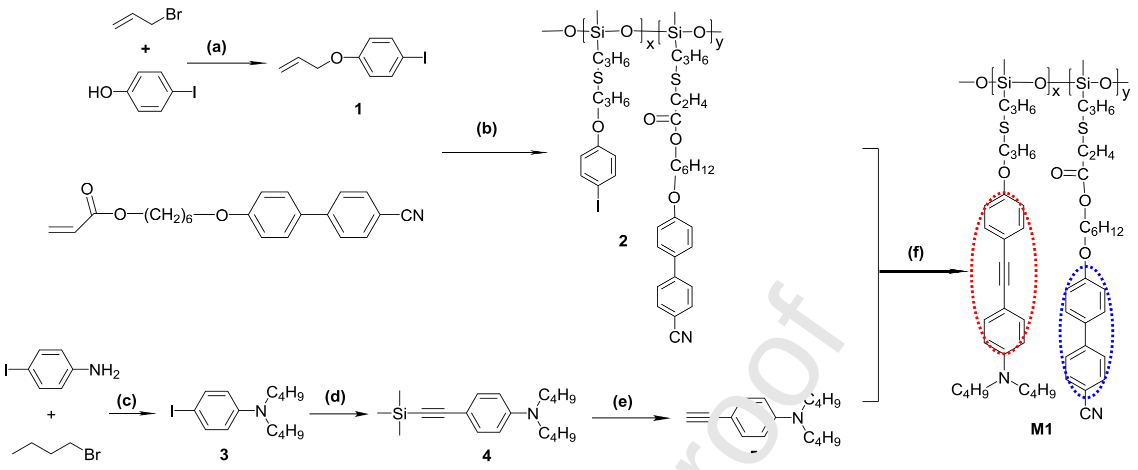


Figure 3. Synthesis of monomer **M1** (a) K_2CO_3, Acetonitrile, 85°C, 3 h; (b) DMPA, THF, 365 nm UV, 30 min; (c) K_2CO_3, KI, DMF, 120°C, Ar, 20 h; (d) TMSA, $PdCl_2(PPh_3)_2$, CuI, TEA, THF, 40°C, Ar, 8 h; (e) K_2CO_3, THF, MeOH 25°C, 3 h; (f) CuI, $PdCl_2(PPh_3)_2$, THF, TEA, 40°C, Ar, 8 h.

3. Results and discussion

3.1 Polymer Synthesis

The synthesis of polysiloxane polymer **M2** mainly consists of two steps. In the first step, the prerequisite polymer **M1** was synthesized by thiol-ene addition reaction with DMPA as initiator.[28] In the second step, the partial side chain of **M1** reacted with the click reagent F_4-TCNQ through [2 + 2] click chemical reaction to obtain **M2**. As shown in Figure 3, 1-(allyloxy)-4iodobenzene and AC-6CN were grafted onto the main chain PMMS (Poly[3-mercaptopropylmethyl-siloxane]) by UV polymerization. In order to ensure the complete consumption of -SH, the method of step-by-step polymerization was uesd: the dosage of the two reactants was determined according to the molar ratio and then the 1-(allyloxy)-4-iodobenzene was UV-polymerized. After that the excess

AC-6CN was added to the mixture and continued UV polymerization for 30 min. -SH bond can be completely reacted. In addition, the monomer **5** was synthesized by methylsilyl protection, and then reacted with polymer **2** by sequential Sonogashira cross-coupling to form a side chain with an electron donating triple bond.[29]

The chemical structure of the polymer was confirmed by FT-IR and ^{1}H-NMR spectroscopy. The ^{1}H-NMR spectra of AC-6CN, **1**, **5** and **M1** are shown in Figure 4. (The ^{1}H-NMR spectra of **M2** shows in s1) On the basis of the integral ratio of the methylene protons (0.72-0.60 ppm, $Si{-}CH_2{-}$) of PMMS with the aromatic proton (6.92-7.04 ppm) of AC-6CN and the aromatic proton (6.52-6.60 ppm) of the aniline derivative. The actual graft density can be calculated to give a result of around 100%; the -SH bond was substantially eliminated. Terminal olefin proton peaks of AC-6CN and 1-(allyloxy)-4-iodobenzene (**1**) at 5.82-6.51 ppm and 5.25-6.15 ppm were not observed in the ^{1}H-NMR spectrum of **M1**. The terminal acetylene proton peak at 2.98 ppm of the small molecule N, N-dibutyl-4-ethynylaniline (**5**) also did not appear in the **M1** which means that the monomer has been successfully grafted onto the PMMS backbone and all unreacted monomers have been removed. All proton peaks have a good correspondence with the nuclear magnetic spectrum. It is convinced that the thiol-ene click chemistry is a simple and efficient method to graft mesogens onto polysiloxane backbone.

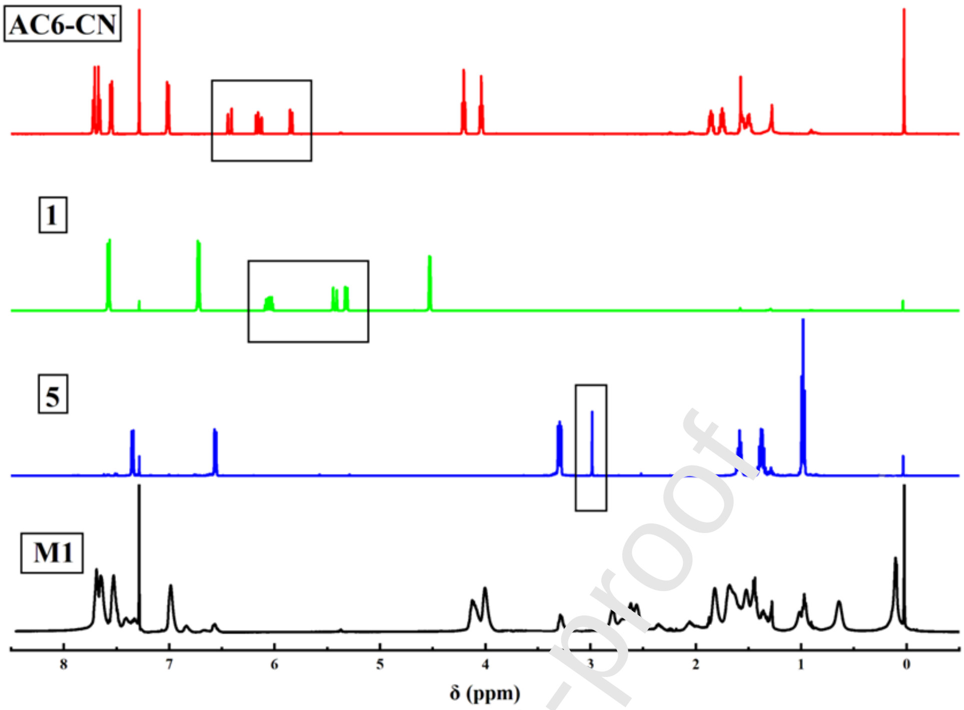


Figure 4. ^{1}H NMR spectra of AC-6CN, **1**, **5** and **M1**.

Figure 5 (a) shows the FT-IR spectrum of PMMS, polymers **M1** and **M2**, there was no absorption at 2557 cm^{-1} for **M2** assignable to the -SH stretching, indicating that the -SH has been completely reacted. The absorption for **M1** in the 2190-2230 cm^{-1} was assignable to the intense stretching vibration of -CN and RC≡CR. After the [2 + 2] click reaction, the peak of this range was replaced by the more intense 2196 cm^{-1} (assigned as the -CN) stretching vibration peak. In addition, the partially amplified FT-IR spectra as shown in Figure 5 (b). The appearance of the vibrational bands, which were derived from ester carbonyl (C=O), N-C and Si-C at 1732 cm^{-1}, 1491 cm^{-1} and 1246 cm^{-1} providing evidence that the preparation of polymers via thiol-ene addition reaction went to completion.

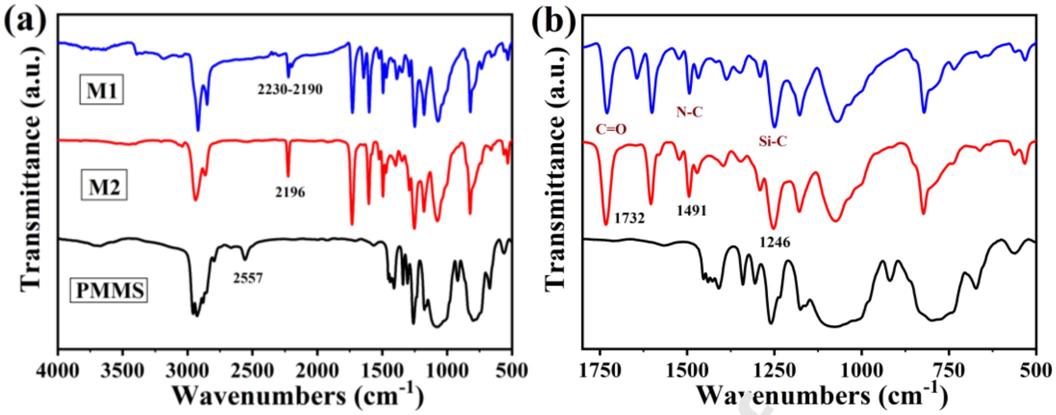


Figure 5. FT-IR spectra of **M1**, **M2** and **PMMS**.

3.2 UV and thermal performance characterization

A side chain liquid crystal polymer **M2** having near-infrared absorption characteristics was prepared by [2 + 2] click chemical reaction, as shown in Figure 6(a). Click chemistry has excellent reactivity and no by-product characteristics. By clicking chemical method, **M2** has both near-infrared absorption and can be well compatible with liquid crystals compared to other materials. **M2** is added as an infrared absorber to the liquid crystal system, so that the system has a good near-infrared absorption effect.

Figure 6 (b) shows the UV-vis absorption spectra of the polymers **M1** and **M2**. **M1** and **M2** showed the same two peaks at 232 nm and 298 nm that are represented by the absorption peak of the siloxane backbone and the absorption peak of AC-6CN. **M1** has a small absorption peak at 342 nm and this peak is expressed as the absorption peak of the aniline derivative branch. The end absorption of the product **M2** after the click chemistry reaction was at 864 nm. It indicates that the click reaction causes the end absorption (λ_{end}) of **M1** to red shift due to the formation of the donor-acceptor chromophore. This also proves that **M2** has a certain absorption under near-infrared light. To investigate the thermal stability of **M2**, TGA and DSC measurements were taken at a scan rate of 10°C · min^{-1} under a nitrogen atmosphere. As shown in Figure 6

thermal tuning of cholesteric liquid crystal

(c) and Table 1, **M2** has good thermal stability and the 5% decomposition temperature ($T_{5\%}$) in nitrogen is higher than 250°C. The polymer has a lower glass transition temperature; this is likely due to the low transition temperature of the polysiloxane system itself. The GPC data of **M2** are shown in Table 1 and Figure s2.

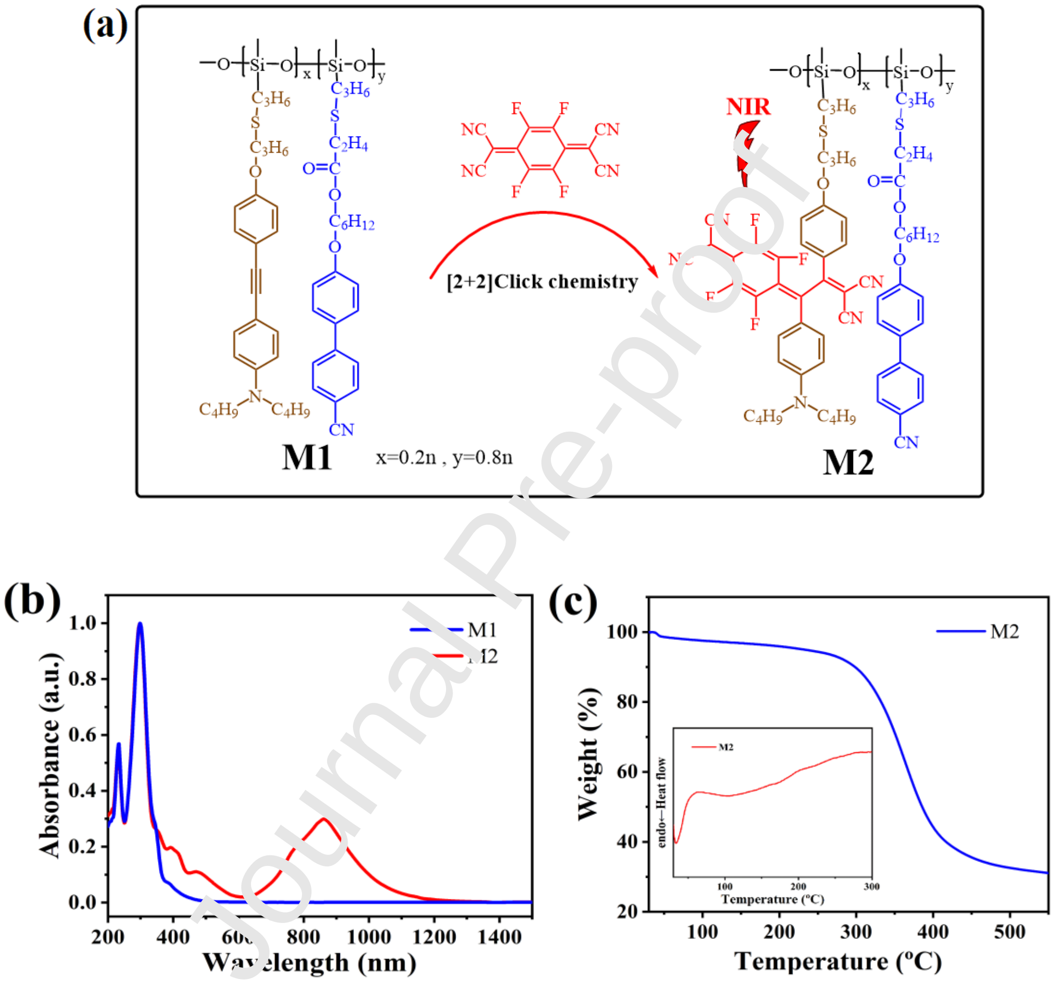


Figure 6. (a) Synthesis of the postfunctionalization by addition of F_4-TCNQ for **M1**; (b) Normalized UV-vis spectra of **M1** and **M2**; (c) TGA of **M2** at the heating rate of 10 °C · min^{-1} under flowing nitrogen.

Table 1 Summary of molecular weights and thermal properties

polymer	M_n[a]	M_w[a]	M_w/M_n[a]	T_g[b]/°C	$T_{5\%}$[c]/°C	$T_{10\%}$[c]/°C
M2	3500	4600	1.31	34	231	298

[a] Determined by GPC in THF using polystyrene standards

thermal tuning of cholesteric liquid crystal

[b] Glass transition temperature determined by the second heating scan of DSC measurements at the scanning rate of 10 °C · min^{-1}

[c] 5% and 10% weight loss temperatures determined by TGA at the heating rate of 10 °C · min^{-1}

3.3 Photo-responsive characterization

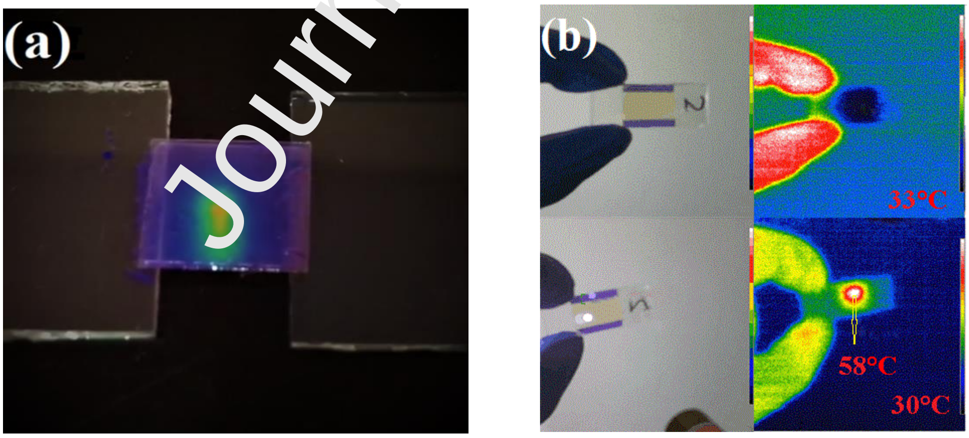
For practical applications, thermal tuning is quite complicated and difficult. Using the CLC mixture, it was demonstrated that the goal can also be accomplished with NIR light. As shown in Figure 7 (a), a polyethylene terephthalate (PET) film was used as a base material to make cells flexible. The prepared CLC mixture (93 wt% SLC1717, 6 wt% CD, 1 wt% **M2**) was injected into two PET films. Prior to irradiation, the cells were purple at room temperature (33°C). When the cells were exposed to 808 nm NIR light at an intensity of 50 mW · cm^{-2}, the color of the irradiated portion rapidly changed. This shows the feasibility of near-infrared light tuning. Cholesteric liquid crystals (CLC) have a certain sensitivity to temperature, but this sensitivity is not obvious and requires high temperature and response time. The addition of the near-infrared dye **M2** and the temperature-sensitive chiral dopant CD alters the temperature sensitivity of the CLC mixture and promotes the photothermal effect of the CLC system.

To further demonstrate the thermal effect of the CLC mixture, a thermal imaging test was performed at room temperature. As shown in Figure 7 (b), the CLC mixture was injected into the liquid crystal cell and handheld thermal imager was used to photothermize the liquid crystal cell. In the absence of NIR light, the thermal imager showed no heat absorption in the cells. When the cell was illuminated with an 808 nm infrared laser, there was a significant hot spot in the cell thermography photograph, demonstrating the great photothermal sensitivity of the CLC mixture. Due to the strong

thermal tuning of cholesteric liquid crystal

absorption of near-infrared light by **M2**, the temperature in the vicinity of the light irradiation is remarkably increased.

Figure 7 (c) is a polarized photograph of the CLC mixture in a liquid crystal cell with different near-infrared illumination time. The inner surfaces of all liquid crystal cells are oriented with PVA solution. It can be seen from the polarized photo that dye **M2** and chiral dopant CD have good solubility in the CLC system, and the system still exhibits a relatively stable planar texture as increasing illumination time. SLC1717 has a high phase transition temperature that allows us to maintain a stable liquid crystal system in the near-infrared external illumination. As shown in Figure 7 (d), the LC phase of the CD/SLC1717/**M2** mixture was characterized using DSC, and only one exothermic peak belonging to the conversion of the cholesteric phase to the isotropic phase was observed above 80 °C during heating and cooling. This indicates that the liquid crystal system has a high definition bright spot and the CLC system can be maintained for a long time under illumination conditions.



thermal tuning of cholesteric liquid crystal

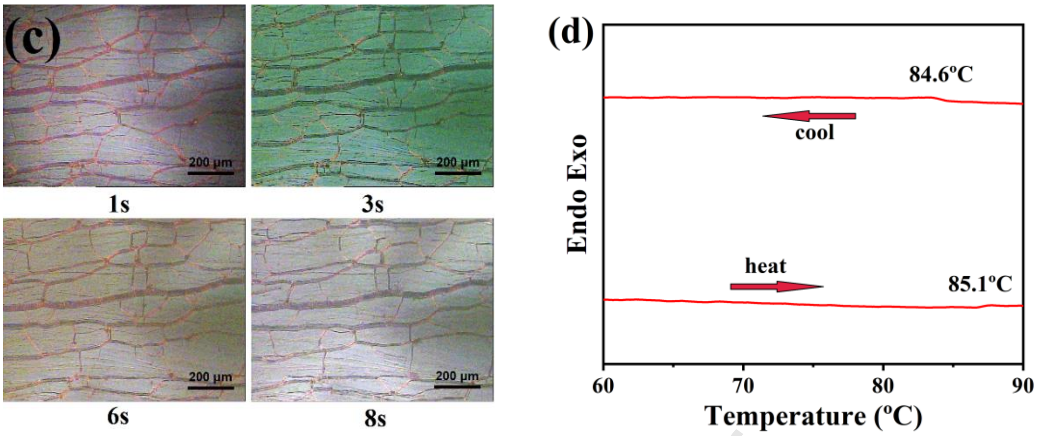


Figure 7. (a) Real cell images created by NIR control of the helices in the CLC to show patterns of RGB colors with a black background in 5 μm thick PET cells (1.0 cm × 1.0 cm); (b) Schematic diagram of thermal imaging of CLC mixture before and after NIR illumination; (c) POM pictures of CLC mixture at different illumination times from 1s to 8 s with a 100-fold objective lens; (d) DSC curve of the **M2**/CD/SLC1717 mixture at a 5°C · min^{-1} cooling rate.

Encouraged by the appropriate HTPs remarkable variation, the selective reflection of CLC in visible spectrum region was demonstrated. CLC mixture was capillary filled into a 5 μm thick PET cell that was black background on one side to create a contrast with a bright iridescent Bragg reflective color from the CLC when viewed from the other side of the cell. The reflection color of 6 wt% chiral dopant CD in SLC1717 was dark purple at the cell and was tuned from blue to green and yellow upon 808 nm light irradiation (50 mW · cm^{-2}) in 8 s (Figure 8a). The whole process responds quickly, and after the light stops, the color of the cells can be restored to dark purple.

HTP value of chiral dopant CD with temperature can be calculated from the relationship between CLC reflection locations and temperature. As can be seen from Figure 8 (b), the weight concentrations of the chiral dopant CD is 6 wt% and the

thermal tuning of cholesteric liquid crystal

transmission peaks locate at 420 nm, 440 nm, 460 nm, 476 nm, 486 nm and 508 nm when the temperature of the chiral dopant are 30, 40, 50, 60, 70 and 80 °C, respectively. The transmittances of curves within the bandwidth are both close to 45%. With the increasing temperature of chiral dopant CD in the LC host of SLC-1717, the regions of transmission shift to longer wavelengths. The HTP value of the chiral dopant can be calculated according to Equations (1) and (2):

$$p = [(HTP) \cdot X_c]^{-1} \tag{1}$$

$$\lambda = n \cdot p \tag{2}$$

Here, p is the pitch of Ch-LC. X_c is the weight concentration of chiral dopant. λ is the reflection bandwidth. n is the average birefringence of the LC.[27] The results are shown in figure 8(c). The results show that the helical twisting force of the chiral dopant CD decreases with increasing temperature, the pitch of the CLC system is increasing and the transmission curve is red-shifted.

Figure 8 (d) shows that the reflective notch of the CLC system varies with increasing 808 nm NIR (50 mW · cm^{-2}) illumination time. The extended illumination causes the reflective notch to move toward longer wavelengths due to the strong absorption of near-infrared light by **M2**; the reduction of the twisting force of the CD helix caused by the conversion of NIR light into heat. The photothermal tuning range is in the range of 400-550 nm over the entire illumination time range. The reversibility and repeatability of the light responsive properties have been proved. The transmission pattern of the sample after 50 cycles of exposure and the relationship between transmission and time after the sample was cooled were measured. The results show that the test samples have good reversibility and repeatability. The results are shown in support information. (Figure s3)

thermal tuning of cholesteric liquid crystal

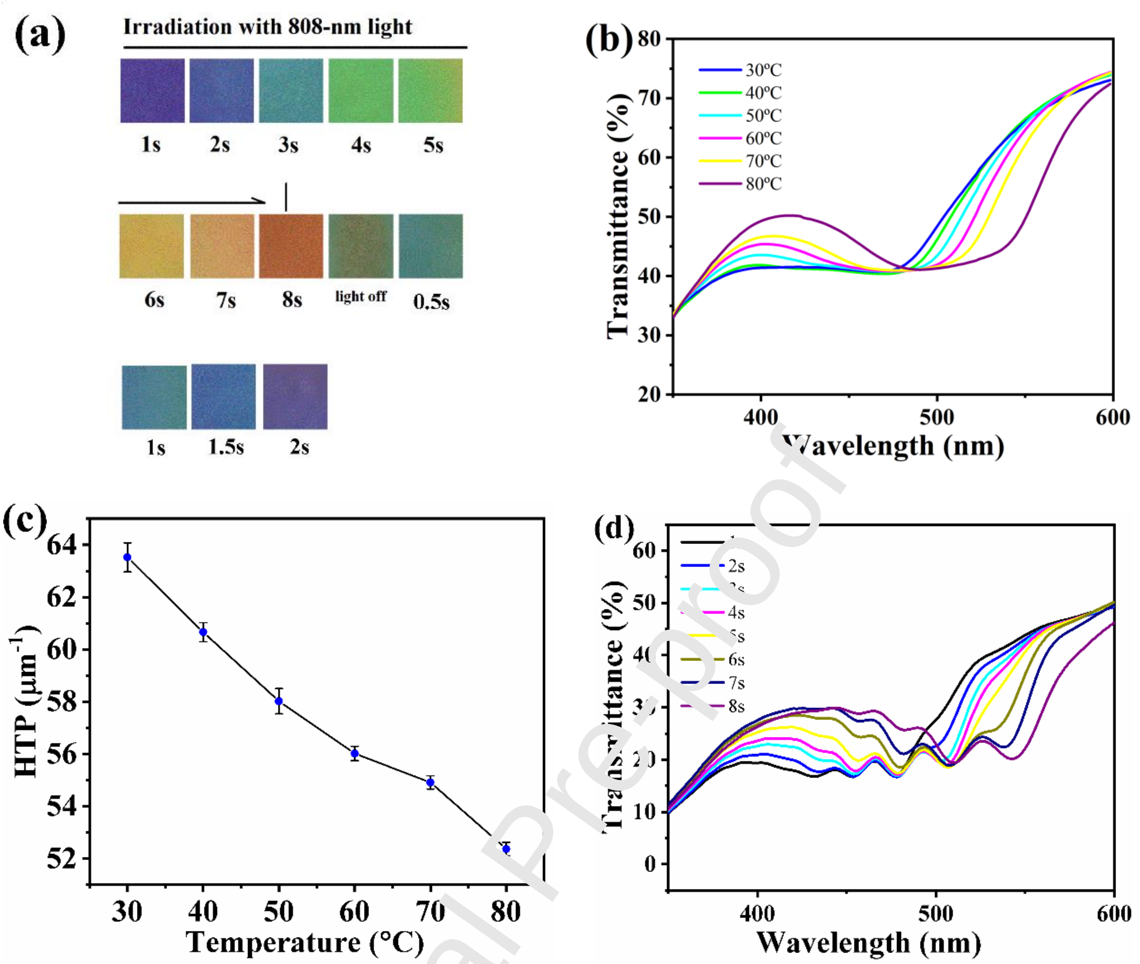


Figure 8. (a) Reflection color images of 1% **M2** in LC host SLC1717 in a 5 μm thick PET cell (1mm x 1mm) upon exposure to 808 nm light (50 mW · cm^{-2}); (b) The CLC cell (CD 6 wt%) transmission spectra as functions of temperature; (c) HTP value of chiral dopant CD with temperature; (d) The CLC cell transmission spectra of 808 nm light at different irradiation times.

Here, we draw a schematic diagram of the CLC system, as shown in Figure 9. The pitch of the portion of the cholesteric liquid crystal in the system that is irradiated with near-infrared light becomes large. Based on the selective reflection of cholesteric liquid crystals, the wavelength of the reflected light changes that in turn shows a different color. This is because the absorption of near-infrared light by **M2** causes the local temperature of the CLC system to rise, so that the helical twisting force of the CD

thermal tuning of cholesteric liquid crystal

decreases and the pitch of the system becomes larger. Different color displays can be obtained by adjusting the NIR illumination time.

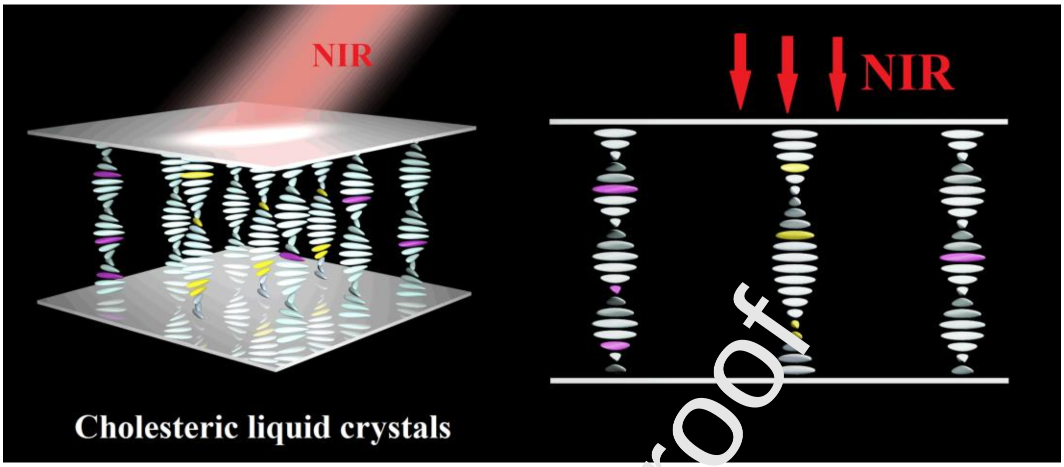


Figure 9. Schematic illustration of the self- organized helical superstructures in the cholesteric LCs tuned by NIR light.

4. Conclusions

In summary, it is feasible to control the reflective notch of the CLC system by NIR light. We designed and synthesized the near-infrared absorbing dye **M2** by double-click reaction. **M2** has good solubility and strong near-infrared absorption characteristics in a liquid crystal system. The entire CLC system produces intense photothermal effects through near-infrared illumination and has a better stability. The thermal effect of excitation by near-infrared light changes the helical twisting force of the CD to cause selective emission of the CLC system. This work has proven to be fast and efficient and provides a new idea for the design of infrared absorbing dyes and the future application of display and inspection systems.

Acknowledgements

thermal tuning of cholesteric liquid crystal

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thermal tuning of cholesteric liquid crystal

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thermal tuning of cholesteric liquid crystal

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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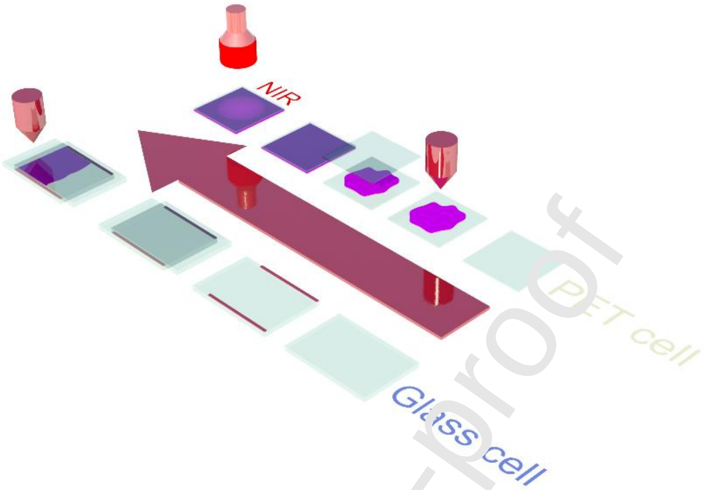
Graphical Abstract



A novel polymer near-infrared dye is used for photothermal tuning of cholesterol liquid crystals. Cholesterol liquid crystal system changes color through near-infrared light exposure. The CLC system has good near-infrared absorption, fast light response and a wide adjustable range.

thermal tuning of cholesteric liquid crystal

Highlights

1 Polymer dye with near-infrared absorption properties was synthesized by thiol-ene click polymerization and [2 + 2] click reaction.

2 Temperature-sensitive chiral dopant changed it spiral twisting force with temperature.

3 Polymer dye and chiral dopant had good solubility in the cholesteric liquid crystal system.

4 The entire cholesteric liquid crystal system achieved photothermal tuning by NIR light.