SUPPORTING INFORMATION

Photoresponsive Liquid Crystalline Polymer Single-Chain Nanoparticles

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1. Synthesis of Monomers and Polymer Precursor

Synthesis of Azobenzene and Coumarin monomers

The coumarin monomer (7-(2-Methacryloyloxyethoxy)-4-methylcoumarin) and azobenzene monomer (6-[4-(4-methoxyphenylazo)phenoxy]hexylmethacrylate) were synthesized according to literature methods and all analysis results are consistent with those previously published.[S1,S2]

Synthesis of Polymer Precursor PAzoMACMA

Ethyl-2-bromoisobutyrate (4.33mg, 0.022mmol), 6-[4-(4-methoxyphenylazo)phen-oxy]hexylmethacrylate (792mg, 2mmol), 4-methyl-[7-(methacryloyl)oxy- ethyloxy] coumarin (64mg , 0.22mmol), PMDETA (10µL, 0.05mmol), Cu(I)Br (7.15mg, 0.05mmol) and 2.5ml of anisole were added under N_2 atmosphere into a round-bottom flask. Then, the mixture was degassed three times using the freeze-pump-thaw procedure and sealed under vacuum. After 30 min stirring at room temperature, the flask was placed in a preheated oil bath (80 °C) for 6 h. The solution was passed through a neutral Al_2O_3 column with THF as eluent to remove the catalyst. The polymer was collected by precipitation twice into hexane. The product was collected and dried in vacuum oven at 25 °C for 24 h, yielding 0.47 g yellow solid (yield: 55%). M_n=10900 g mol^{-1}，M_w=13400 g mol^{-1} and Đ=1.2 (from triple SEC: size exclusion chromatograph).
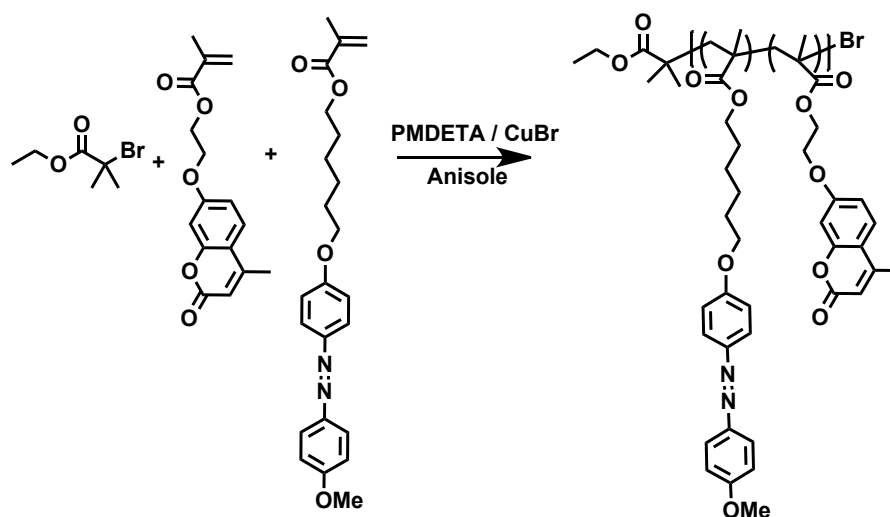
Scheme S1: Synthesis of PAzoMACMA polymer precursor

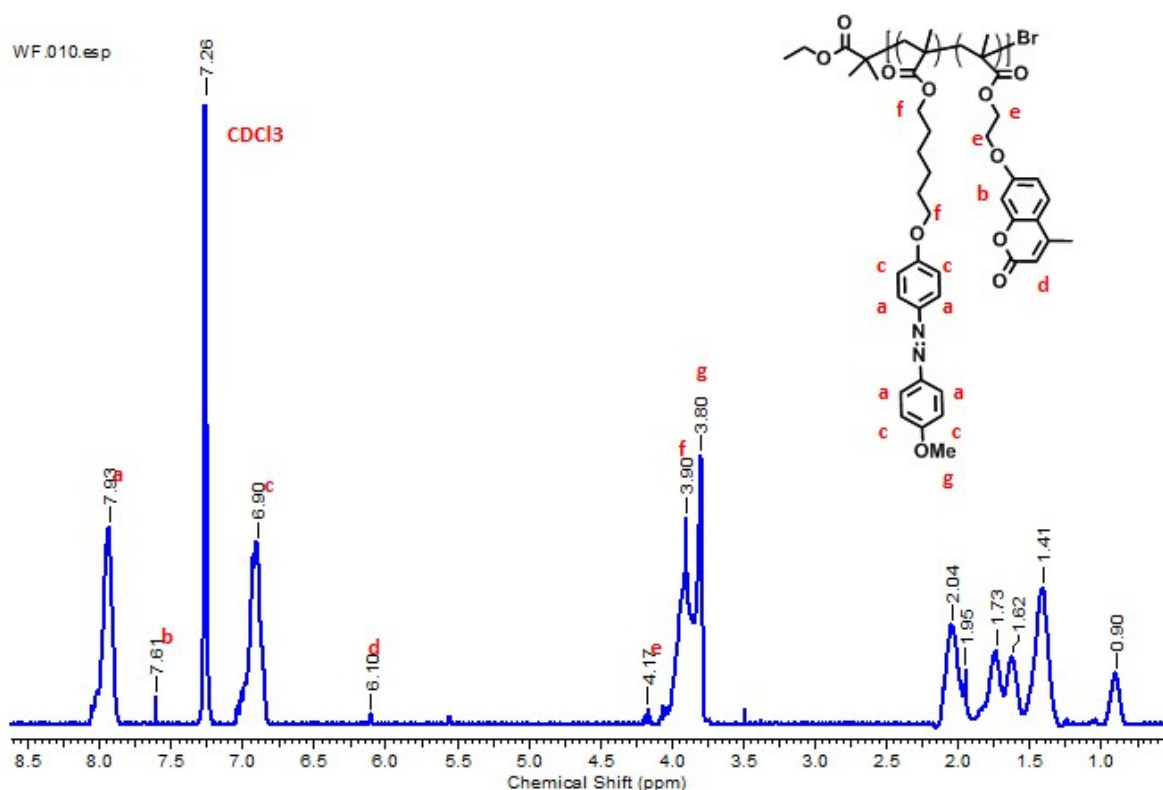**Figure S1:** ^{1}HNMR spectrum of PAzoMACMA in CDCl$_3$.

2. Preparation of Single-Chain Nanoparticles

To fabricate the liquid crystalline (LC) SCNPs, the copolymer PAzoMACMA (2 mg) was dissolved in THF (10 mL), and the solution was kept under stirring overnight. After being filtered with a 200nm pore size Teflon membrane, the solution was exposed to 320-480 nm UV light for 30min. The solution was concentrated under vacuum distillation and the polymer nanoparticles were then precipitated in hexane, collected and dried under vacuum overnight. The LC-SCNPs could be re-dispersed in THF or CHCl$_3$ to form a homogenous solution with a desired concentration. The photodimerization of coumarin in PAzoMACMA solution (0.2 mg/mL, THF), which is responsible for intra-chain crosslinking, was monitored using UV-vis absorption spectra recorded from a solution upon 320-480 nm UV irradiation for varying times. The obtaining of LC-SCNPs was confirmed by using SEC. The dilute LC-SCNP solution was directly injected into the column of SEC for the measurement after photodimerization of coumarin groups.

3. Optical behavior of Single-Chain Nanoparticles

The trans-cis photoisomerization of azobenzene mesogens in LC-SCNPs was investigated using UV-vis spectroscopy with a dilute solution in THF (0.2 mg/mL). Unless otherwise stated, the solution was exposed to 365nm UV light for 5min for the trans-cis isomerization and subsequently to 400-500nm visible light for 5min for the cis-trans back isomerization. In case CHCl$_3$ was used as the solvent, the

LC-SCNP solution was irradiated under 365nm UV light for 15min to obtain the cis isomers of azobenzene and then heated to 75°C for 1h in water bath to get the maximum azobenzene back to the trans form. The photoluminescence of LC-SCNPs in $CHCl_3$ was measured with azobenzene in different isomerization states and various excitation wavelengths (365nm or 460nm) were used for recording the emission spectra. The preservation of LC order in LC-SCNPs was investigated by means of differential scanning calorimetry (DSC) under a heating or cooling rate of 10 °C min^{-1} and polarizing optical microscope (POM). The sample under POM observation was heated to 185 °C, then decrease the temperature from 185 °C to 110 °C at 0.2 °C/min and keep in 110 °C for 72hrs.

4. Photoinduced Deformation of Single–Chain Nanoparticles

Photoinduced deformation of LC-SCNPs was examined using AFM. To prepare the sample, a THF solution was cast onto the surface of mica; after removing THF the LC-SCNPs were subjected to either of the two irradiation procedures. In the first one, the sample was heated at 115°C and was pretreated by unpolarized UV light (365nm) irradiation for 15min. Then the sample was irradiated under linearly polarized visible light (400-500nm) for 15min at 115°C in the isotropic phase for equilibrium and keep irradiation until being cooled to room temperature. In the second one, similarly the sample was first irradiated under unpolarized visible light (400-500nm) for 15min at 115°C, to reach the maximum amount of azobenzene trans isomers for pretreatment and then was exposed to linearly polarized UV light (365 nm) for 15min at 115°C and continuously irradiation until being cooled to room temperature.

5. Nanocomposite Preparation and Characterization.

To prepare thin films of the PMMA/LC-SCNP nanocomposite, PMMA dissolved in 1,2-dichloroethane (0.5g/mL, 10mL) was mixed with LC-SCNPs dissolved in chloroform (5mg/mL in 5mL). The homogenous solution was then cast on a microscope slide to form a film after drying in a vacuum oven. To investigate the possibility of aligning the LC-SCNPs upon film elongation, the nanocomposite film was stretched at 113 °C (above Tg of PMMA) to either 400% strain at a rate of 25mm/min, followed by rapid cooling under strain at room temperature. Polarized UV-vis spectroscopy was utilized to characterize the orientation.

6. Instruments and Measurements

^{1}H NMR spectra were recorded on a Bruker (400MHz) spectrometer with $CDCl_3$ as the solvent at 293 K. The chemical shifts were referenced to residual peaks of solvent: $CDCl_3$ (7.26 ppm). Size exclusion chromatography (SEC) measurements were performed on an Agilent 1260 Infinity SEC system with MDS multi detectors (UV detector, RI detector, Viscometer and Dual Angle LS detector: 15° and 90°). Tetrahydrofuran (THF) was used as the eluent at a flow rate of 0.4 mL/min at 30°C. The SCNPs were

prepared via intra-chain crosslinking of polymer precursor under UV irradiation from an OmniCure@ Series 1000 UV lamp with 320-480nm filter (240mW/cm^2 at 350nm, 5cm distance). The photoisomerization of azobenzene were excited using the same lamp with 365nm filter for UV light (65 mW/cm^2, 5cm distance) and 400-500nm filter for visible light (115mW/cm^2 at 440nm, 5cm distance). The power of irradiation was measured by ORIEL 70260 Radiant Power Meter. The photodimerization of coumarin and photoisomerization of azobenzene were monitored by recording UV-vis spectroscopy on a Varian 50 Bio UV-vis spectrophotometer. Transmission Electron Microscopy (TEM) measurements were performed with a Hitachi H-7500 instrument at a voltage of 80 kV. The specimen was prepared by drop-casting the sample solution onto a carbon-coated copper grid, followed by drying at room temperature. Atom Forced Microscopy (AFM) measurements were performed on a Dimension Icon AFM instrument equipped with a NanoScope V controller (Veeco/Digital Instruments, Santa Barbara, CA). AFM topographical images were done under ScanAsyst mode at room temperature using a silicon nitride (force constant 0.4 N/m) cantilever tips. The thermal phase transition behavior was investigated by Q-200 differential scanning calorimeter (DSC) from TA Instruments, using indium as the calibration standard. Polarizing optical microscopic (POM) observations were carried on a Leitz DMR-P microscope equipped with an Instec hot stage. Steady-state fluorescence emission and excitation spectra were recorded on a Varian Eclipse fluorescence spectroscopy. The PMMA/SCNP nanocomposite films were stretched by using an Instron 5965 universal testing system. A load cell of 500N was fitted into the instrument and the tensile tests were performed at a speed of 25 mm/min in 113 °C.

7. Triple detection SEC results of PAzoMACMA polymer precursor and SCNPs
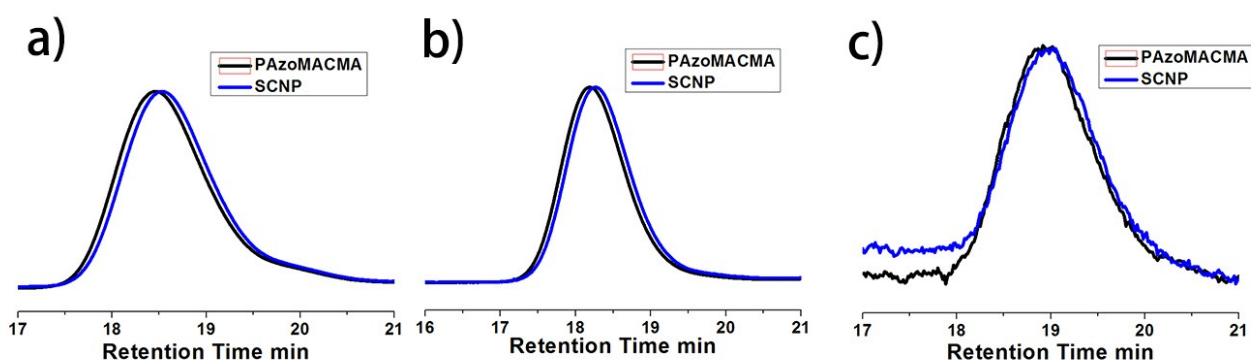

Figure S2: SEC traces of PAzoMACMA polymer precursor and SCNPs, a) Refractive Index (RI) detection traces. b) Light scattering (LS) detection traces (15°). c) Viscometric (VS) detection traces

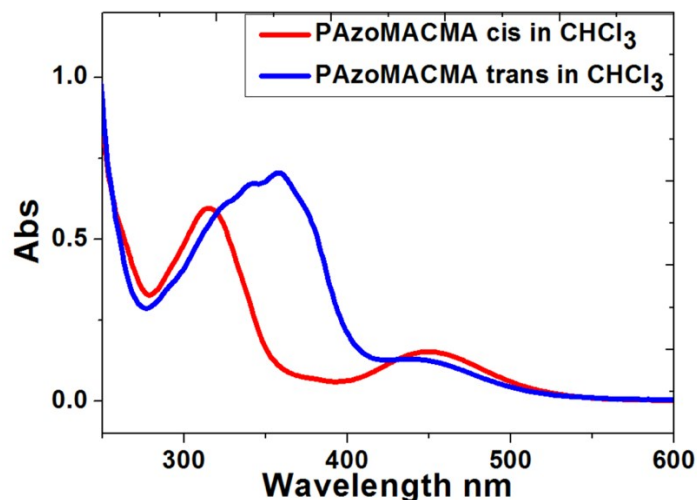## 8. UV-vis spectra and photoisomerization of PAzoMACMA polymer precursor in CHCl$_3$

Figure S3: UV-vis absorption spectra of PAzoMACMA polymer precursor in CHCl$_3$ in the rich-in-cis state after 365nm UV irradiation for 15 min and in the subsequent rich-in-trans state after 400-500nm visible light irradiation for 15min.

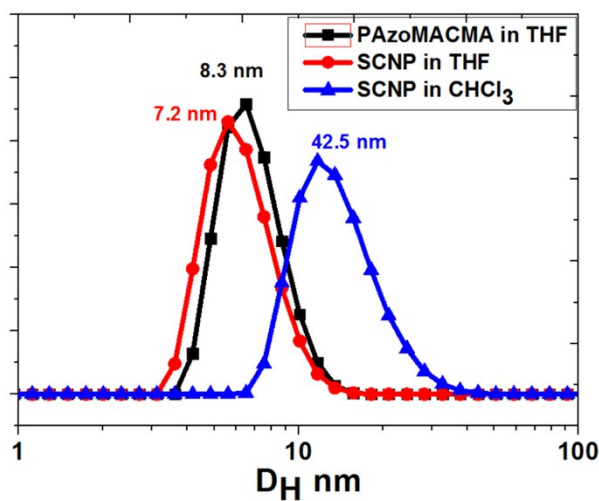## 9. DLS results of PAzoMACMA polymer precursor and SCNPs

Figure S4: DLS results of linear polymer precursor of PAzoMACMA in THF and SCNPs in both THF and CHCl$_3$.
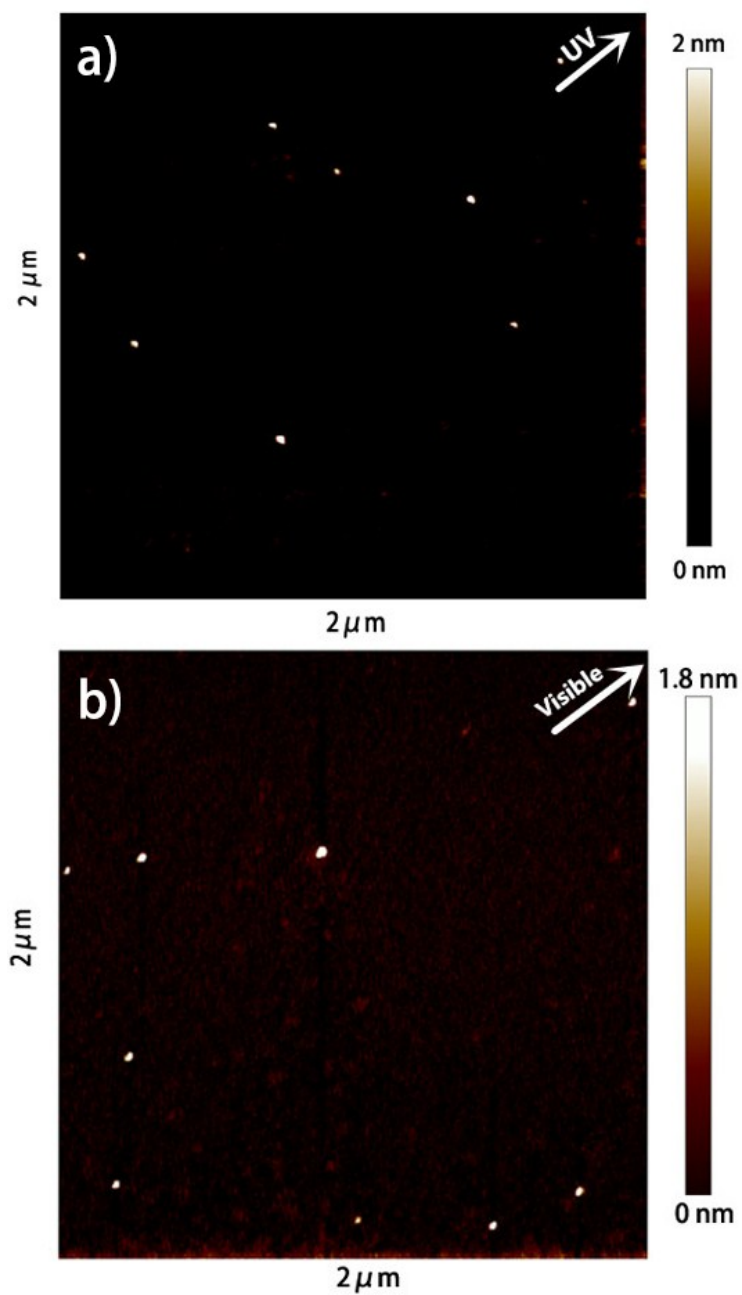
10. Photo-induced deformation of SCNPs

Figure S5: AFM images of deformed SCNPs under linearly polarized UV (365nm) (a) and visible light (400-500nm) irradiation (b). The arrow indicates the light polarization direction.

References

(S1) J. Jiang, B. Qi, M. Lepage, Y. Zhao; *Macromolecules*, 2007, **40**, 790-792

(S2) X. Tao, Z. Guo, T. Satoh, Y. Cui, T. Kakuchi, Q. Duan; *Polym. Chem.*, 2011, **2**, 2068