Supporting Information

Reusable gold nanorod/liquid crystalline elastomer (GNR/LCE) composite films with UV-triggered dynamic crosslinks capable of micropatterning and NIR actuation

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S1. Preparation of gold nanorods (GNRs)

S1.1 Preparation of monodisperse GNRs stabilized by CTAB, denoted as CTAB-GNRs

Monodisperse gold nanorods (GNRs) stabilized by cetyltrimethyl ammonium bromide (CTAB) were synthesized referring to a seed mediated growth method as reported by Murray group.[1] All glassware were washed with aqua regia and dried in an oven at 120 ^{o}C overnight before use.

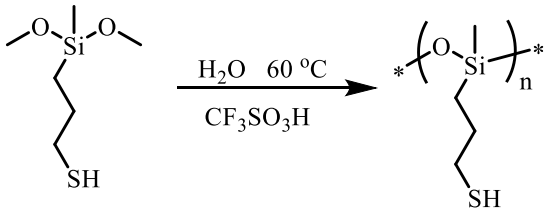
The seed solution preparation: 5 mL of $HAuCl_4$ solution (0.5 mM) was mixed with 5 mL of CTAB solution (0.2 M) in a 20 mL glass vial. Then 0.6 mL of fresh ice-cooled $NaBH_4$ aqueous solution (0.01 M) was quickly injected into the above vial with vigorous stirring (1200 rpm). The mixture solution color changed from yellow to brownish-yellow instantly, and the stirring was stopped after 5 min. The obtained mixture solution was further aged at room temperature for 60 min before used as the seed solution.

The second step is the preparation of growth solution: In a 500 mL Erlenmeyer flask, 9.02 g CTAB and 1.1 g 5-bromosalicylic acid were dissolved in 250 mL warm water (~ 60 ^{o}C). After the mixture solution was cooled down to 30 ^{o}C, a 12 mL of $AgNO_3$ solution (4.0 M) was added into the flask under slow stirring (400 rpm), then the system was left undisturbed for 15 min at 30 ^{o}C. Then, 250 mL $HAuCl_4$ solution (1.0 mM) was added and the whole mixture solution turned golden yellow. After slow stirring (400 rpm) for 90 min, 2.0 mL of ascorbic acid solution (0.06 M) was added, and then vigorouly stirred for 30 s until the solution became colorless.

Preparation of GNRs stabilized by CTAB: A 0.4 mL portion of the seed solution made in the previous step was injected into the above growth solution, the resultant mixture solution was stirred vigorously for 30 s and then left undisturbed for 12 h at room temperature for the growth of GNRs, the prepared CTAB-stabilized aqueous dispersed GNR solution demoted as CTAB-GNRs was left standing still for further use or for the following ligand exchange.

S1.2 Preparation of organic solvent dispersible GNRs stabilized by thiol side-group PMMS *via* ligand exchange method

S1.2.1 Synthesis of poly(3-mercaptopropylmethylsiloxane) (PMMS) with thiol side-groups



Scheme S1 Polymerization route of poly(3-mercaptopropylmethylsiloxane) (PMMS) with thiol side-groups from 3-mercaptopropylmethyldimethoxysilane.

The synthesis of poly(3-mercaptopropylmethylsiloxane) (PMMS) was according to a modified literature procedure.[2] To a 100 mL round bottom flask equipped with an addition funnel and a stirring bar, 3-mercaptopropylmethyldimethoxysilane (20 g, 0.039 mmol) and deionized water (5 mL) was added with vigorously stirring for 4 h under nitrogen at 60 ^{o}C. Then the water and methanol were removed with heating to 80 ^{o}C under reduced pressure, a prepolymer of poly(3-mercaptopropylmethylsiloxane) was obtained as colorless liquid (16.7 g).

Then trifluoromethanesulfonic acid (0.2 mL) was added and heated to 100 ^{o}C, reaction for 24 h under vigorous stirring. After added with diethyl ether (50 mL), the solution was washed with water until the pH of aqueous layer became 7. The collected organic layer was dried over sodium sulfate and then concentrated through rotary evaporation. After removing all the residual reactants and other impurities through heating at 150 ^{o}C under reduced pressure, the polymer PMMS with thiol side-groups was harvested as a colorless liquid (13.26 g, 79.6% yield). $M_{n,GPC}$ = 2800 g/mol, PDI = 1.70. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.60-2.55 (m, 2H), 1.70-1.60 (m, 2H), 1.38 (s, -SH), 0.68-0.58 (m, 2H), 0.15-0.05 (s, 3H).

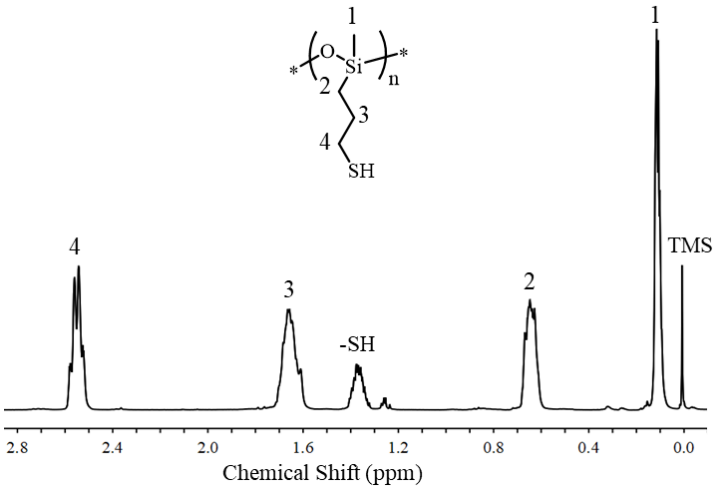


Fig. S1 ^{1}H NMR spectrum of poly(3-mercaptopropylmethylsiloxane) (PMMS) with thiol side-groups.

S1.2.2 Preparation of monodisperse GNRs stabilized by PMMS, denoted as PMMS-GNRs

To convert the aqueous dispersed CTAB-GNRs into organic solvent dispersible GNRs, the GNRs stabilized by poly(3-mercaptopropylmethylsiloxane) (PMMS) with thiol side-groups were prepared by a ligand exchange procedure,[3] thus obtained product was denoted as PMMS-GNRs.

First, 8.0 mL of the above prepared aqueous dispersed CTAB-GNRs solution was pipetted into a centrifuge tube (25 mL), after centrifugation at 8000 rpm for 10 min, the isolated GNRs were re-dispersed in 10.0 mL of deionized water and carried out centrifugal separation once again. The above centrifugation-redispersion procedure was repeated for three times and finally the harvested GNRs were dispersed in 2.0 mL water. The typical TEM image of the aqueous dispersed CTAB-GNRs is shown in Fig. S2a, which exhibited uniform sizes (48 ± 5 nm in length, 14 ± 1 nm in width) and displayed n LSPR peak at 793 nm and a transverse plasmon resonance peak at 510 nm (Fig. S2b).

In the next step, 0.05 g PMMS was dissolved in 2.5 mL toluene, and the obtained solution was then added slowly into the above freshly prepared aqueous dispersed

CTAB-GNRs solution (2 mL). After that, 4 mL acetone was slowly added and the mixture was vigorously stirred at room temperature for 5 min. Then, after the upper organic layer was carefully separated and centrifugated at 10000 rpm for 10 min, with removal of the supernatant, the obtained raw product of PMMS-GNRs was re-dispersed in 2.0 mL anhydrous THF and carried out centrifugation once again. The above centrifugation-redispersion procedure was repeated for three times and the harvested organic solvent dispersible PMMS-GNRs were steadily dispersed in 2.0 mL anhydrous THF, with the concentration of gold was determined to be $C_{Au} = 3.02 \times 10^{-9}$ mol/L based on ICP-MS measurements.[3] Typical TEM images (Fig. S2c) confirmed the monodisperse characteristics of PMMS-GNRs in THF solution (50 ± 5 nm in length, 16 ± 1 nm in width), and the corresponding LSPR peak of GNRs/THF solution blue-shifted to 781 nm (Fig. S2d), which may be caused by the slightly increased sizes of GNRs during the ligand exchange coated with PMMS.

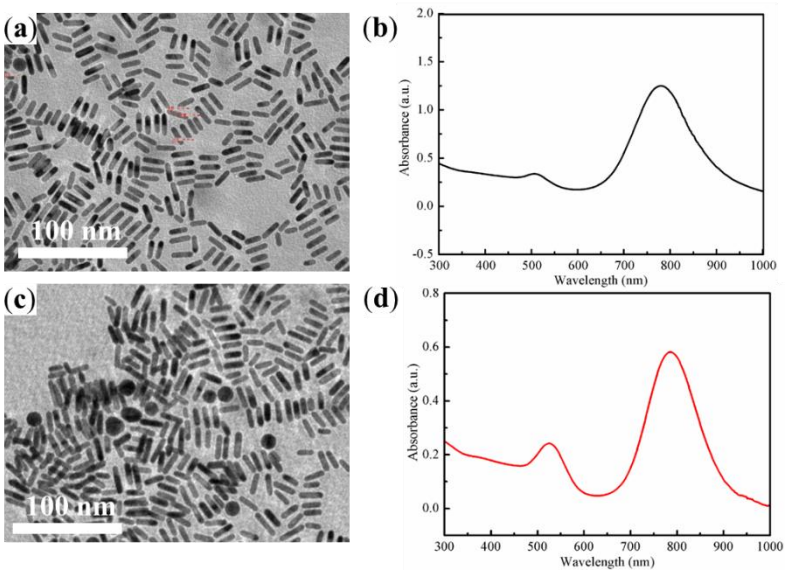
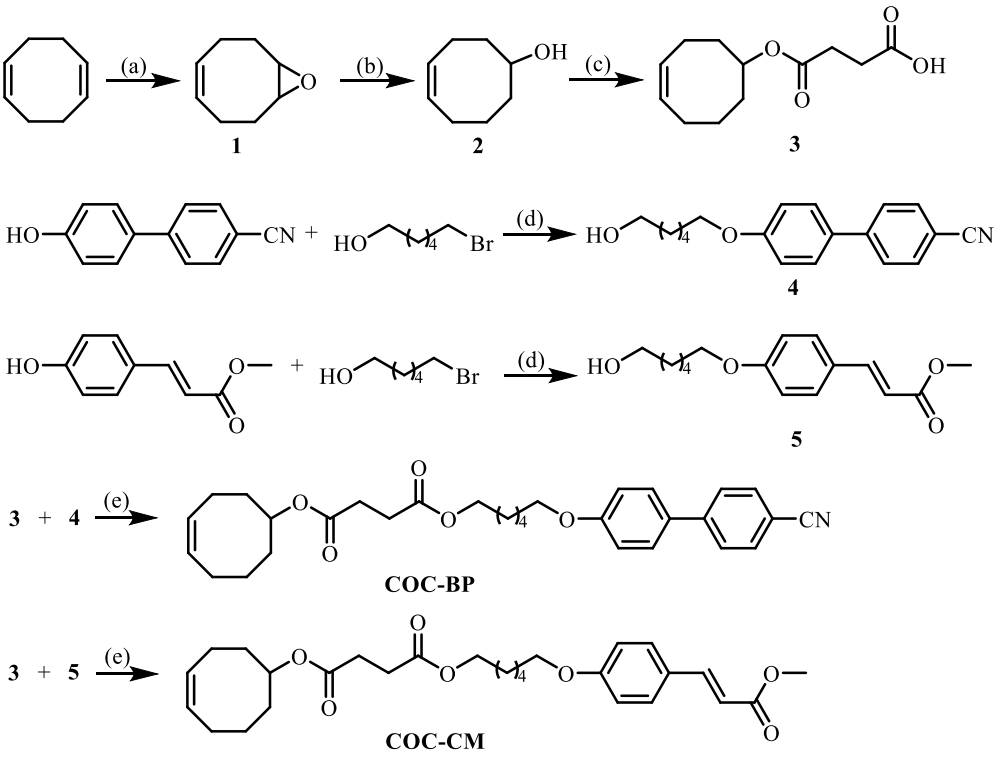


Fig. S2 (a, c) TEM images and (b, d) UV-vis spectra for (a, b) the aqueous dispersed CTAB-GNRs, and (c, d) the organ soluble PMMS-GNRs.

S2. Synthesis of cyclooctene monomers



Scheme S2 Synthesis route for the cyclooctene monomers COC-BP with biphenyl (BP) mesogens and COC-CM with cinnamate (CM) groups. Reaction conditions: (a) *m*-CPBA, $CHCl_3$, N_2, 0 ^oC to r.t., 12 h; (b) $LiAlH_4$, THF, N_2, 0 ^oC to r.t., 12 h; (c) Succinyloxide, DMAP, toluene, reflux, 16 h; (d) K_2CO_3, KI, acetone, 80 ^oC, 48 h; (e) DMAP, DCC, CH_2Cl_2, r.t., 48 h.

Synthesis and characterization of cyclooctene monoepoxide **1**

The synthesis of cyclooctene monoepoxide **1** was according to a modified literature procedure.[4] To a 250 mL round bottom flask equipped with an addition funnel and a stirring bar was added *cis*-1,5-cyclooctadiene (5.29 g, 48.9 mmol, 1.0 eq.) and $CHCl_3$ (10 mL). With the flask cooled in an ice bath, a solution of *m*-chloroperbenzoic (*m*-CPBA, 85%, 12.00 g, 59.1 mmol, 1.2 eq.) in $CHCl_3$ (100 mL) was added dropwise over 2 h. The reaction mixture was warmed to room temperature and allowed to stir overnight. The precipitated solid was removed by sucking filtration and the organic filtrate was washed with saturated aqueous $NaHCO_3$ solution (3×100 mL). The collected organic layer was dried with sodium sulfate and then concentrated by rotary evaporation. The crude product was purified by flash chromatography on a silica gel column with petroleum: ethyl acetate = 10:1 to afford cyclooctene monoepoxide **1** as

a colorless liquid (4.31g, 34.8 mmol, 71.1% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.50 (t, 2 H), 3.13-2.98 (m, 2 H), 2.63-1.83 (m, 8 H).

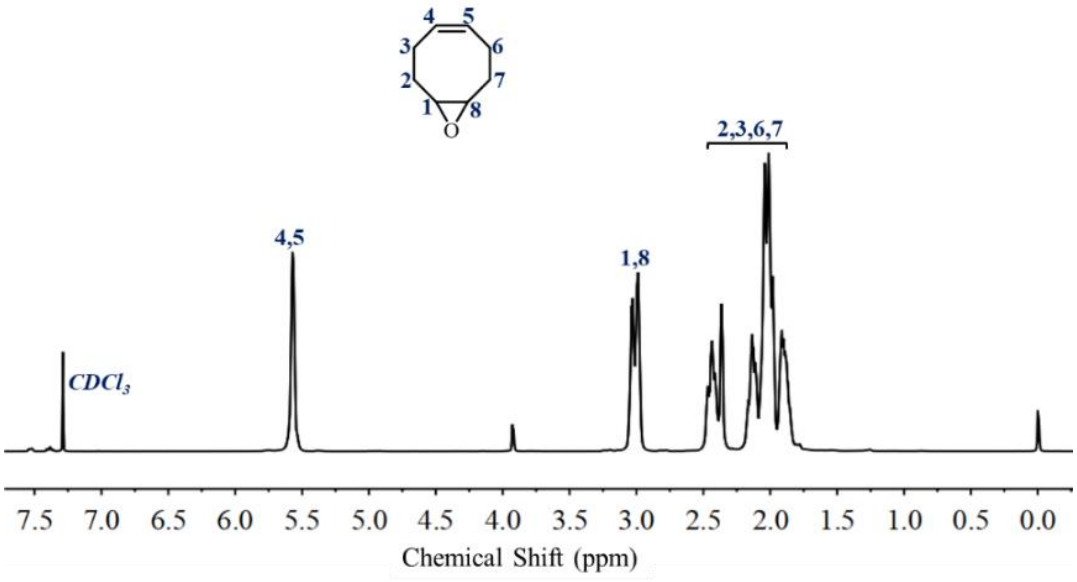


Fig. S3 ^{1}H NMR spectrum of compound **1** in $CDCl_3$ at room temperature.

Synthesis and characterization of monohydroxy cyclooctene **2**

The synthesis of monohydroxy cyclooctene **2** was referring to a modified literature procedure.[4] To a dry three-neck round bottom flask (100 mL) equipped with a stirring bar, septum, and reflux condenser was added lithium aluminum hydride powder ($LiAlH_4$) (1.14 g, 30.0 mmol, 1.5 eq.) under nitrogen atmosphere. With the flask cooled in an ice bath, dried THF (30 mL) was added to dissolve $LiAlH_4$. To this reaction slurry with vigorous stirring was slowly added cyclooctene monoepoxide **1** (2.50 g, 20.0 mmol, 1.0 eq.) dissolved in dried THF (30 mL). The reaction mixture was warmed up to room temperature and allowed to stir overnight. With the flask cooled in an ice bath once again, water (0.9 mL), a solution of 10% aqueous sodium hydroxide (0.9 mL), and additional water (2.7 mL) were added dropwise to the slurry in turn. This mixed solution was allowed to stir for another 4 h to quench the reaction, during which time the gray salts slowly became white. Afterwards, the salts were filtered and the filtrate was dried over sodium sulfate. The solution was concentrated by rotary evaporation and then purified by flash chromatography on a silica gel column with petroleum: ethyl acetate = 7:3 to afford cycloct-4-enol **2** as a colorless oil

(2.30 g, 18.22 mmol, 91.1% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.74-5.55 (m, 2 H), 3.80 (m 1 H), 2.38-1.45 (m, 10 H).

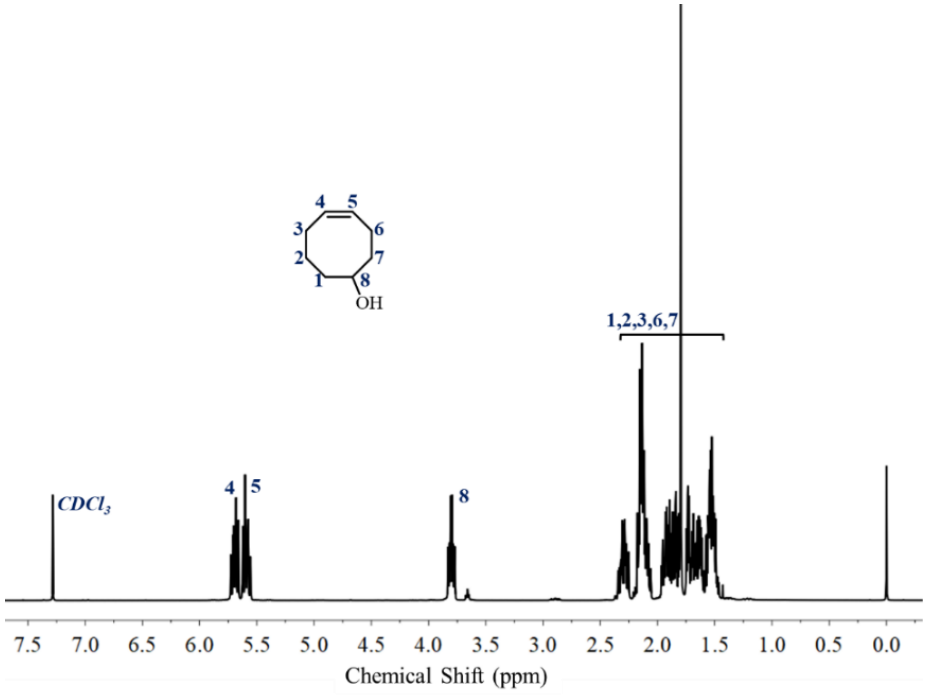


Fig. S4 ^{1}H NMR spectrum of compound **2** in $CDCl_3$ at room temperature.

Synthesis and characterization of succinic acid mono-4-cycloocten-1-yl ester **3**

The synthesis of succinic acid mono-4-cycloocten-1-yl ester **3** was according to a modified literature procedure.[5] To a 50 mL round bottom flask equipped with a stirring bar was added cycloct-4-enol **2** (2.77 g, 22.0 mmol, 1.1 equiv), succinic anhydride (2.00 g, 20.0 mmol, 1.0 equiv.), 4-dimethylaminopyridine (DMAP) (48.9 mg, 0.4 mmol, 0.02 equiv.), and anhydrous toluene (20 mL). The reaction mixture was refluxed (110 ^{o}C) for 16 h with a vigorous stirring. After cooling to room temperature, the reaction mixture was washed with 1 M hydrochloric acid solution (2 × 10 mL) and the organic fractions were dried with sodium sulfate and then concentrated by rotary evaporation. The crude product was dissolved in hot ethanol (3 mL) and precipitated in water (50 mL) to afford succinic acid mono-cyclooct-4-enyl ester **3** as a white solid product (4.17 g, 18.4 mmol, 92.2% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.70 (m, 2H), 4.88 (m, 1H), 2.68-2.55 (m, 4H), 2.38-1.52 (m, 10H).

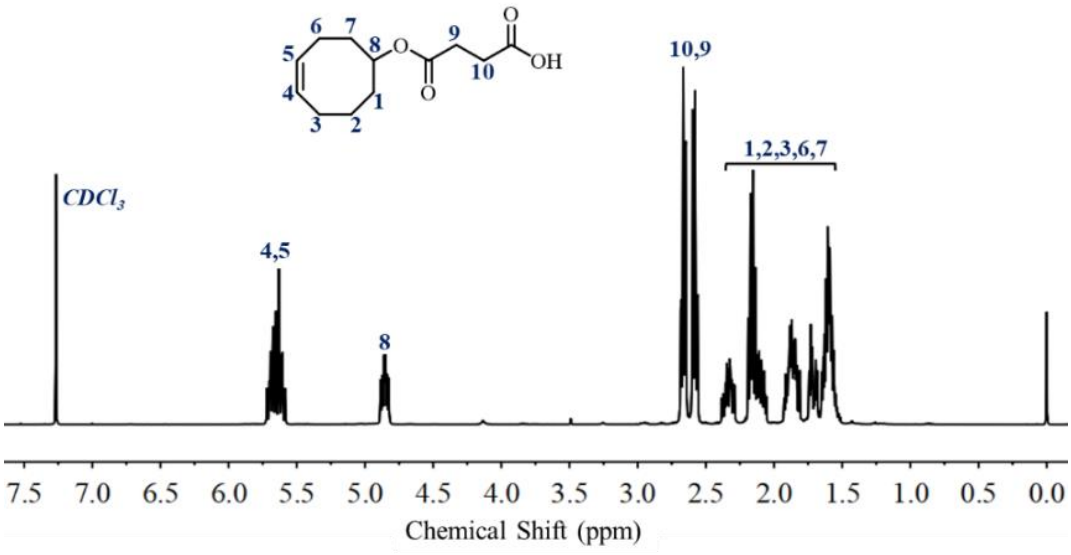


Fig. S5 ^{1}H NMR spectrum of compound **3** in $CDCl_3$ at room temperature.

Synthesis and characterization of 4-(6-Hydroxyhexyloxy)-4'-cyanobiphenyl **4**

The synthesis of 4-(6-Hydroxyhexyloxy)-4'-cyanobiphenyl **4** was referring to a modified literature procedure.[6] To a 500 mL round bottom flask equipped with a stirring bar was added 4-cyano-4'-hydroxybiphenyl (4.88 g, 25.0 mmol, 1.0 equiv.), 6-bromo-1-hexanol (5.43 g, 30.0 mmol, 1.2 equiv.), potassium carbonate (5.18 g, 37.5 mmol, 1.5 equiv.), potassium iodide (0.17 g, 1.0 mmol, 0.04 equiv.), and acetone (200 mL). The reaction mixture was refluxed for 48 h at 80 ^{o}C. After cooling to room temperature, the solid precipitate was filtrated and the organic fractions were concentrated by rotary evaporation. The crude product was purified by flash chromatography on a silica gel column with petroleum: dichloromethane = 5:1 to afford 4-(6-Hydroxyhexyloxy)-4'-cyanobiphenyl **4** as a white solid (5.47 g, 18.5 mmol, 74.0% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71-7.62 (m, 4 H), 7.53 (d, 2 H), 6.97 (d, 2 H), 4.02 (t, 2 H), 3.69 (t, 2H), 1.91-1.39 (m, 8 H).

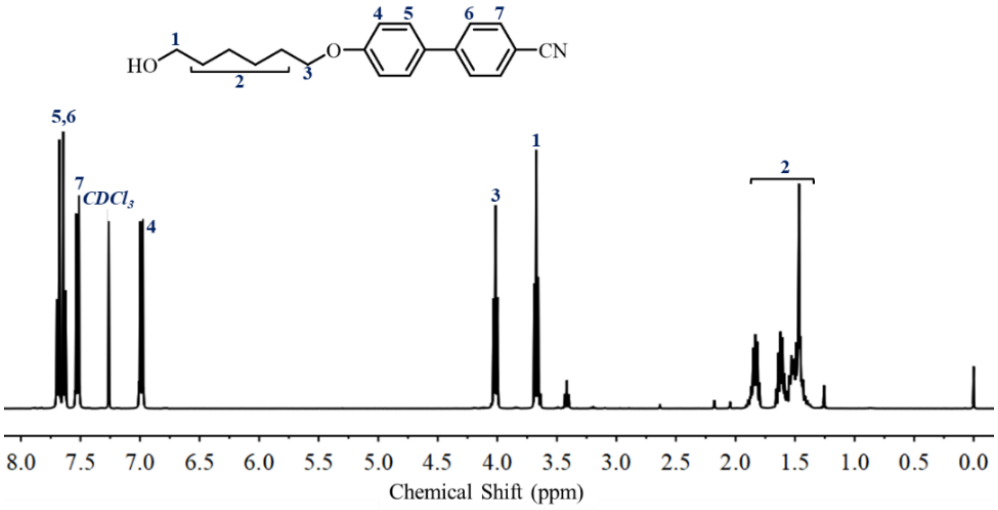


Fig. S6 ^{1}H NMR spectrum of compound **4** in $CDCl_3$ at room temperature

Synthesis and characterization of methyl 4-(6-hydroxyhexyloxy)cinnamate **5**

The synthesis of methyl 4-(6-hydroxyhexyloxy)cinnamate **5** was referring to a modified literature procedure.[6] To a 500 mL round bottom flask equipped with a stirring bar was added methyl 4-hydroxycinnamate (4.45 g, 25.0 mmol, 1.0 equiv.), 6-bromo-1-hexanol (5.43 g, 30.0 mmol, 1.2 equiv.), potassium carbonate (5.18 g, 37.5 mmol, 1.5 equiv.), potassium iodide (0.17 g, 1.0 mmol, 0.04 equiv.), and acetone (200 mL). The reaction mixture was refluxed for 48 h at 80 ^{o}C. After cooling to room temperature, the solid precipitate was filtrated and the organic fractions were concentrated by rotary evaporation. The crude product was purified by flash chromatography on a silica gel column with petroleum: dichloromethane = 5:1 to afford methyl 4-(6-hydroxyhexyloxy)cinnamate **5** (5.29 g, 19.0 mmol, 76.0%yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, 2 H), 7.45 (d, 2 H), 6.88 (d, 2 H), 3.98 (t, 2 H), 3.79 (s, 3 H), 3.68 (t, 2H), 1.90-1.35 (m, 8 H).

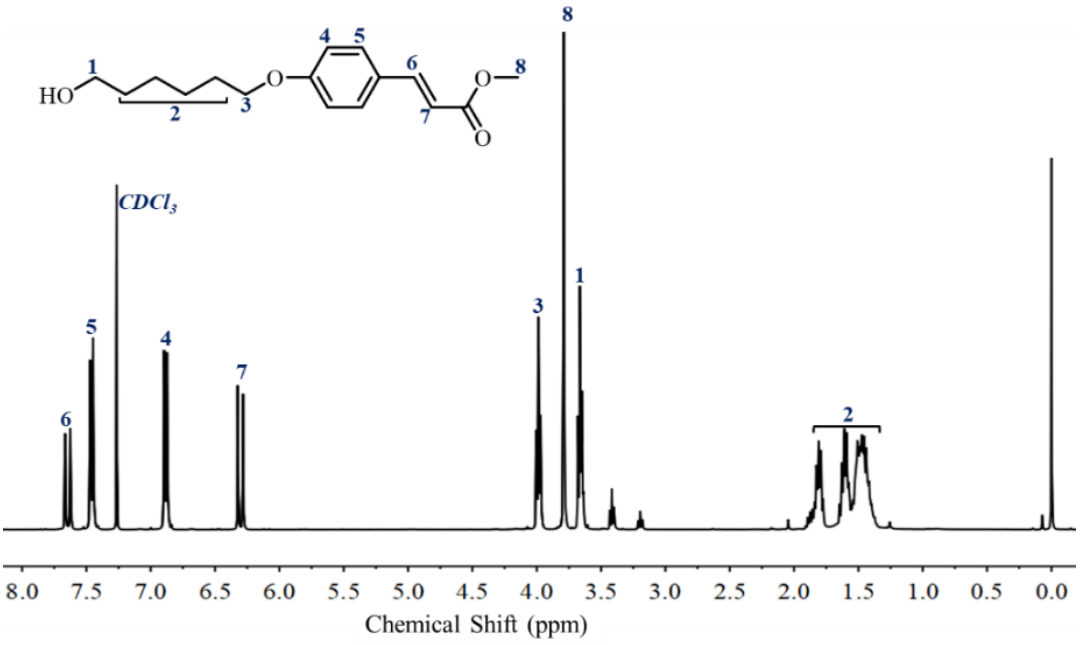


Fig. S7 ^{1}H NMR spectrum of compound **5** in $CDCl_3$ at room temperature

Synthesis and characterization of biphenyl mesogen-based cyclooctene (COC-BP)

The synthesis of biphenyl mesogen-based cyclooctene (COC-BP) was according to a modified literature procedure.[3] To a 500 mL three-neck round bottom flask equipped with a stirring bar was added succinic acid mono-4-cycloocten-1-yl ester **3** (2.71 g, 12.0 mmol, 1.0 equiv.), 4-(6-hydroxyhexyloxy)-4'-cyanobiphenyl **4** (3.54 g, 12.0 mmol, 1.0 equiv.), 4-dimethylaminopyridine (DMAP) (0.29 g, 2.4 mmol, 0.2 equiv.), and dry CH_2Cl_2 (60 mL) under nitrogen atmosphere. With the flask cooled in an ice bath, *N*,*N*-dicyclohexylcarbodiimide (DCC) (2.72 g, 1.1 equiv.) in anhydrous CH_2Cl_2 (50 mL) was added dropwise over 30 min and the reaction mixture was allowed to stir for 36 h under nitrogen. The precipitate was filtrated and the organic fractions were washed with deionized water (3×100 mL). The collected organic layer was dried with sodium sulfate and then concentrated by rotary evaporation. The crude product was purified by flash chromatography on a silica gel column with petroleum: ethyl acetate = 10:1 to afford biphenyl mesogen-based cyclooctene (COC-BP) (3.16 g, 6.3 mmol, 52.3%yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71-7.62 (m, 4 H), 7.53 (d, 2 H), 6.99 (d, 2 H), 5.64 (m, 2H), 4.84 (m, 1H), 4.13-3.98 (m, 4 H), 2.59 (m, 4 H), 2.38-0.83 (m, 18 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.42, 170.57, 158.72, 144.26, 131.54, 130.32,

128.77, 128.56, 127.32, 126.06, 118.08, 114.07, 109.05, 75.04, 66.92, 63.64, 32.67, 32.52, 28.22, 27.52, 24.67, 24.53, 23.78, 21.27.

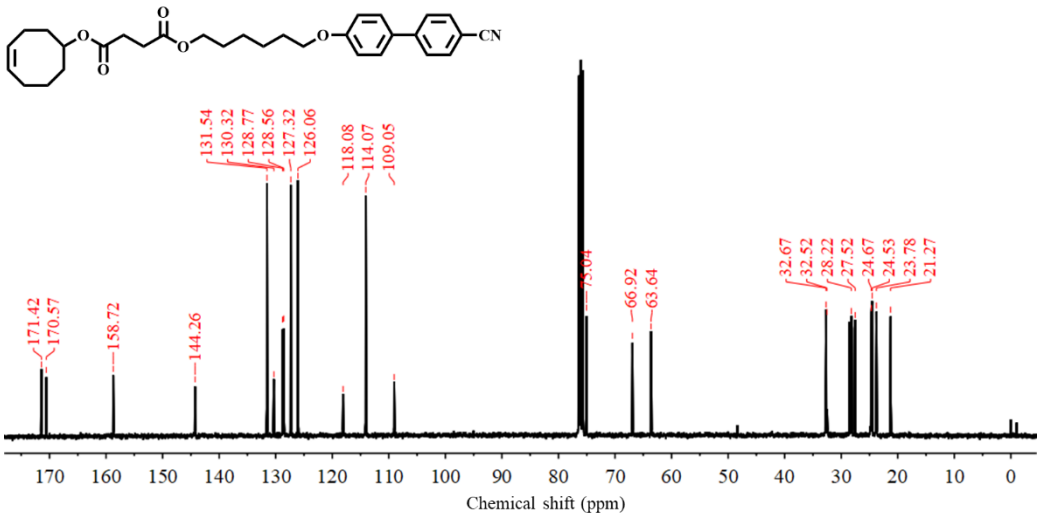


Fig. S8 ^{13}C NMR spectrum of COC-BP in $CDCl_3$ at room temperature

Synthesis and characterization of cinnamate group-based cyclooctene (COC-CM)

The synthesis of cinnamate group-based cyclooctene (COC-CM) was according to a modified literature procedure.[5] To a 500 mL three-neck round bottom flask equipped with a stirring bar was added succinic acid mono-4-cycloocten-1-yl ester **3** (2.71 g, 12.0 mmol, 1.0 equiv.), methyl 4-(6-hydroxyhexyloxy)cinnamate **5** (3.34 g, 12.0 mmol, 1.0 equiv.), 4-dimethylaminopyridine (DMAP) (0.29 g, 2.4 mmol, 0.2 equiv.) and dried CH_2Cl_2 (60 mL) under nitrogen atmosphere. With the flask cooled in an ice bath, *N*,*N*-dicyclohexylcarbodiimide (DCC) (2.72 g, 1.1 equiv.) in anhydrous CH_2Cl_2 (50 mL) was added dropwise over 30 min and the reaction mixture was allowed to stir for 36 h under nitrogen. The precipitate was filtrated and the organic layer was washed with deionized water (3×100 mL). The collected organic layer was dried with sodium sulfate and then concentrated by rotary evaporation. The crude product was purified by flash chromatography on a silica gel column with petroleum: ethyl acetate = 10:1 to afford cinnamate group-based cyclooctene (COC-CM) (2.43 g, 5.0 mmol, 41.7%yield). ^1H NMR (400 MHz, $CDCl_3$): δ 7.65 (d, 2 H), 7.45 (d, 2 H), 6.88 (2, 2 H), 6.30 (d, 2H), 5.63 (m, 2H), 4.84 (m, 1 H), 4.10 (t, 2H), 3.97 (m, 2H), 3.79 (s, 3 H),

2.58 (m, 4 H), 2.38-1.15 (m, 18 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.44, 171.59, 167.81, 160.98, 144.61, 129.80, 129.73, 129.58, 126.97, 115.14, 114.83, 76.06, 67.92, 64.65, 51.57, 33.70, 33.54, 29.55, 28.53, 25.71, 25.55, 24.80, 22.29.

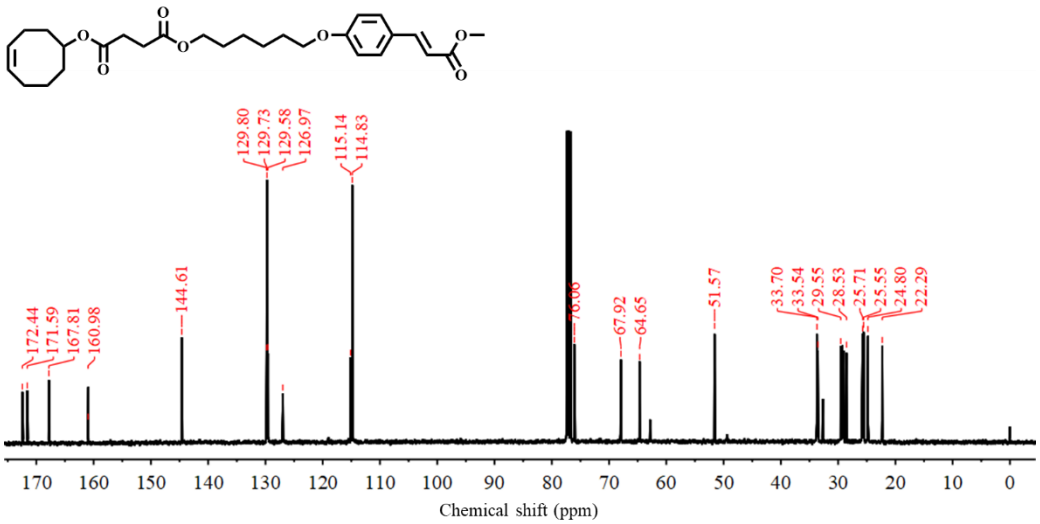


Fig. S9 ^{13}C NMR spectrum of COC-CM in $CDCl_3$ at room temperature

S3. Other supplementary figures

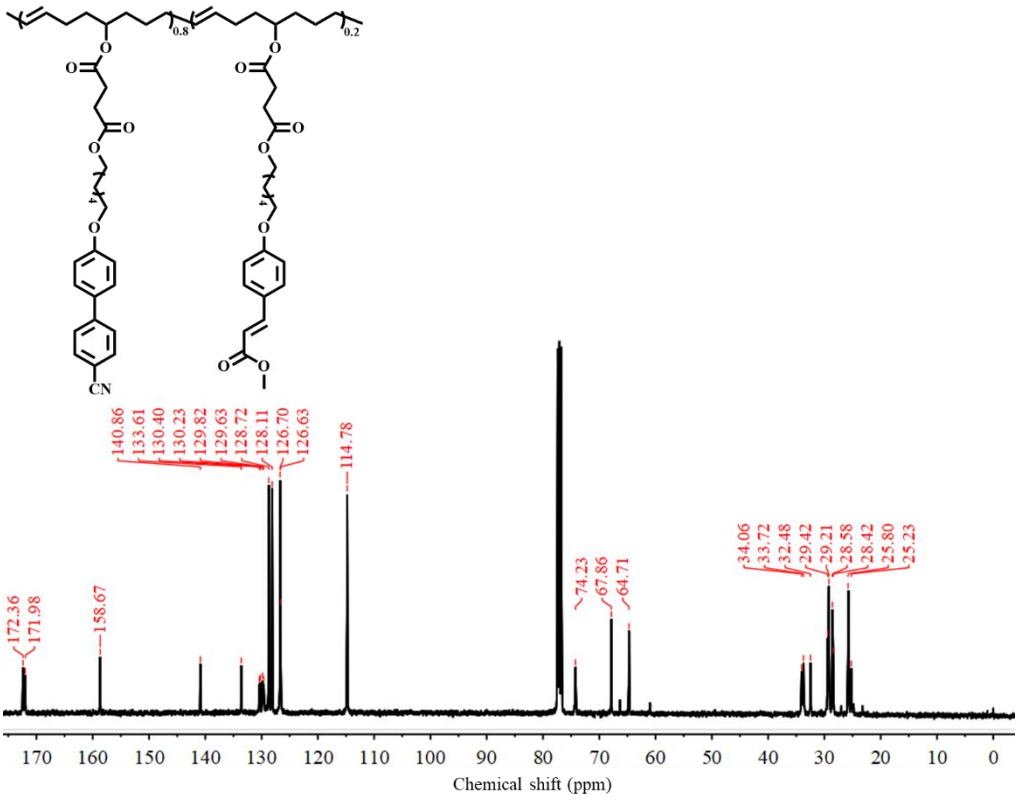


Fig. S10 ^{13}C NMR spectrum of P($BP_{0.8}$-*r*-$CM_{0.2}$) in $CDCl_3$ at room temperature

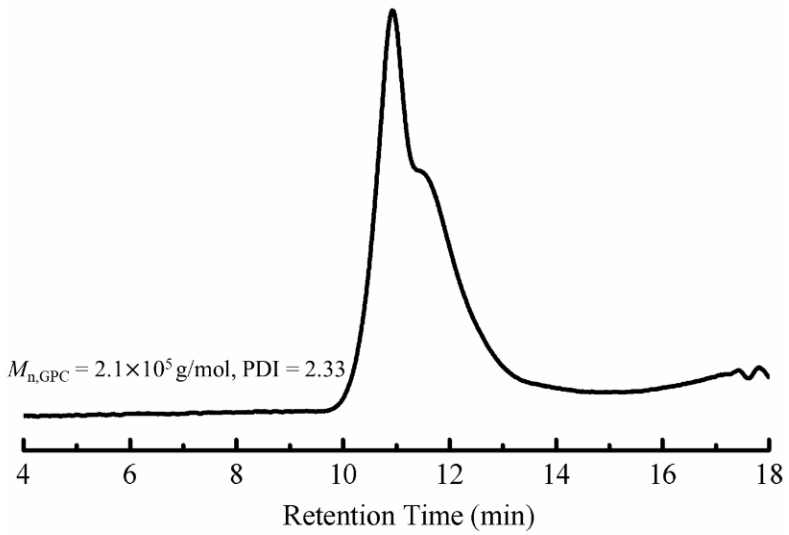


Fig. S11 GPC chromatogram of the copolymer P($BP_{0.8}$-*r*-$CM_{0.2}$). Polymerization conditions: $[COC\text{-}BP]_0$: $[COC\text{-}CM]_0$: [2nd generation Grubbs' catalyst]$_0$ = 350: 85: 1, $n_{COC\text{-}BP}$ = 0.99 mmol, V_{DCM} = 2.0 mL, T = 55 ^{o}C, N_2 atmosphere.

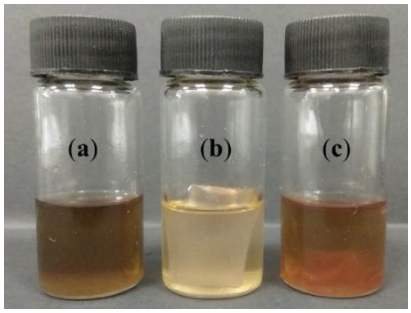


Fig. S12 Gel fraction tests with the same amount of (a) LCE-1, (b) LCE-2, and (c) LCE-3 immersed in THF with fixed volume at room temperature for 12 h to investigate the cross-linking degree and the retrocycloaddition-based de-cross-linking efficiency in our LCE films.

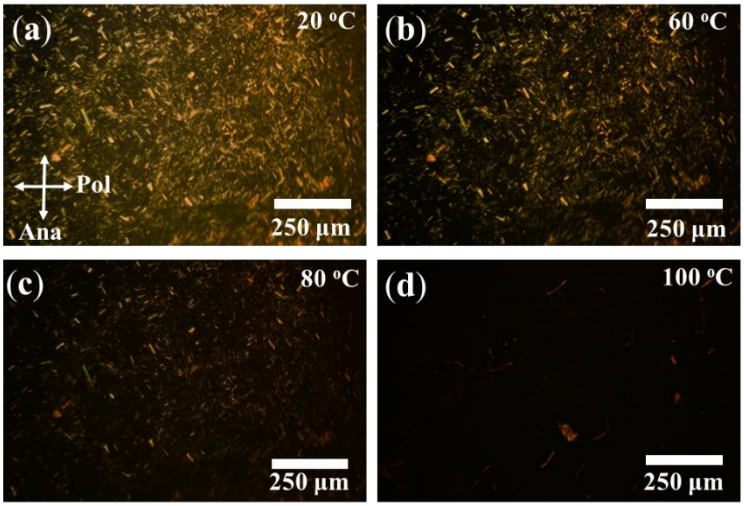


Fig. S13 POM images of a 313 nm UV light-crosslinked GNR/LCE composite film without stretching at different temperature of (a) 20 ^{o}C, (b) 60 ^{o}C, (c) 80 ^{o}C, (d) 100 ^{o}C.

S4. Supplementary references

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