Electronic Supplementary Information (ESI)

High-strength Thermochromic and Mechanochromic Liquid-Crystal Elastomers with Responsive Shape Memory and Dynamic Adhesion

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Characterization

Swelling test*:* The network structures of the CLCE films were characterized by a swelling test. It was carried out by the following steps: the sample was cut into pieces, then swelled by CH_2Cl_2, and extracted at room temperature for 24 h. The masses of the original sample (m_0), the swelled extracted sample (m_s), and the dried extracted sample (m_d) were recorded, respectively. The swelling ratio (S (%)) and gel content (G (%)) were calculated by the following formulas:

$$S(\%) = \frac{m_S}{m_d} \times 100\%$$

$$G(\%) = \frac{m_d}{m_0} \times 100\%$$

Evaluation of shape memory effect for CLCEs:

For triple SME, employing the T_g and $T_{Ch\text{-}I}$ of the networks as transition temperature, three characteristic programming temperatures including T_{low}, $T_{mid,}$ and T_{high} are set at 10 °C, 30 °C, and 120 °C, respectively. Taking $RM_{0.5\%}$-$CLCE_{5\%}$ as an example, in the programming step, for deformation from S0 to S1, the temperature was kept at 120 °C for 3 min to make sure the sample was in the isotropic state, and then the sample was stretched from the original strain (ε_{S0}), cooled to 30 °C under constant stress leading $\varepsilon_{S1,\ load}$. The removal of external stress at 30 °C for an additional 3 min, results in the first temporary shape (ε_{S1}). The fixing of the shape S1 is realized by the orientation of mesogen in CLCEs when the temperature is decreased to the $T_{Ch\text{-}I}$. For further deformation from S1 to S2, the sample is stretched at 30 °C and cooled to 10 °C under constant stress resulting in $\varepsilon_{S2,\ load}$, then unloading the external stress to achieve the second temporary shape (ε_{S2}). The fixing of the shape S2 relies on the vitrification of the backbone of the network when the temperature is lower than T_g. The recovery process is implemented by heating in two steps at stress-free conditions. In the first recovery process from S2→S1, the unconstrained strain recovery is driven by heating the sample to 30 °C, and thermally equilibrated for 5 min which denotes as $\varepsilon_{S1,\ rec}$. Essentially, the stored energy of backbone chains is released when the temperature is beyond the T_g, and the shape S1 recovers by entropic elasticity. In the second recovery process from S1→S0, the permanent shape is finally obtained by further heating to 120 °C, followed by keeping for 5 min. The shape fixity ratio (R_f) and the shape recovery ratio (R_r) can be calculated following the literature method[1].

For two-way SME, different temperature ranges and applied stresses were chosen to study the SME as the phase transition of the CLCEs and mechanical strength with different achiral RM82

content were different. For a clear description ($RM_{0.5\%}$-$CLCE^{5\%}$), a typical test program for a temperature range of 120-10 °C is described as follows. 1) Heat the sample at 120 °C (DMA procedure: equilibrate at 120 °C) and apply stress (0.03 MPa at a rate of 0.005 MPa/min). 2) Cool to 10 °C (DMA procedure: equilibrate at 0 °C) and hold isothermally for 10 min. 3) Maintain stress application and reheat to 120 °C (this is the end of cycle 1). Steps 2) 3) and 4) represent a 2W-SME cycle and can be repeated many times. The absolute strain actuation (R_{act}) and strain recovery ratio (R_{rec}) can be calculated in accordance with the literature method[2].

Supporting Tables:

Table S1. The compositions of CLCEs and the data of swelling tests.

Samples Composition (wt.%)				*S* (%)	*G* (%)
	RM82	mLC	mDK756		
$RM_{0.5\%}$-$CLCE_{5\%}$	0.5	93.5	5	798±36	92±2
$RM_{1\%}$-$CLCE_{5\%}$	1	93	5	678±24	92±1
$RM_{2\%}$-$CLCE_{5\%}$	2	92	5	523±9	92±2
$RM_{4\%}$-$CLCE_{5\%}$	4	90	5	382±3	94±1
$RM_{6\%}$-$CLCE_{5\%}$	6	88	5	326±5	94±1
$RM_{8\%}$-$CLCE_{5\%}$	8	86	5	289±5	95±2
$RM_{10\%}$-$CLCE_{5\%}$	10	84	5	261±7	97±1
$RM_{10\%}$-$CLCE_{4.3\%}$	10	84.7	4.3	260±2	95±1
$RM_{4\%}$-$CLCE_{3.5\%}$	4	91.5	3.5	403±2	93±1
$RM_{4\%}$-$CLCE_{3.8\%}$	4	91.2	3.8	395±2	94±1
$RM_{4\%}$-$CLCE_{4\%}$	4	91.0	4	392±4	94±1
$RM_{4\%}$-$CLCE_{4.3\%}$	4	90.7	4.3	388±1	94±1
$RM_{4\%}$-$CLCE_{4.5\%}$	4	90.5	4.5	385±2	95±1
$RM_{0.5\%}$-$CLCE_{4.3\%}$	0.5	94.2	4.3	746±10	94±1
$RM_{0.5\%}$-$CLCE_{3.5\%}$	0.5	95	3.5	765±25	93±1

Note. The mass ratio of Irg184 was 1% in all compositions.

Table S2. The data of DSC test.

Samples	T_g (℃)	T_{Ch-I} (℃)	ΔH ($J.g^{-1}$)
$RM_{0.5\%}$-$CLCE_{5\%}$	21.3	109.3	3.5
$RM_{1\%}$-$CLCE_{5\%}$	21.6	110.5	3.0
$RM_{2\%}$-$CLCE_{5\%}$	22.7	113.0	2.8
$RM_{4\%}$-$CLCE_{5\%}$	23.0	115.1	2.2
$RM_{6\%}$-$CLCE_{5\%}$	23.6	119.8	1.8
$RM_{8\%}$-$CLCE_{5\%}$	24.8	124.1	/
$RM_{10\%}$-$CLCE_{5\%}$	25.3	131.7	/

Table S3. The data of the stretching test.

Samples	Tensile strengths (MPa)	Elongations (%)
$RM_{0.5\%}$-$CLCE_{5\%}$	7.7±0.5	306±21
$RM_{1\%}$-$CLCE_{5\%}$	9.5±0.3	245±15
$RM_{2\%}$-$CLCE_{5\%}$	13.5±0.6	180±22
$RM_{4\%}$-$CLCE_{5\%}$	16.5±0.3	155±7
$RM_{6\%}$-$CLCE_{5\%}$	17.2±0.3	104±5
$RM_{8\%}$-$CLCE_{5\%}$	18.0±0.1	76±8
$RM_{10\%}$-$CLCE_{5\%}$	19.7±0.1	71±7

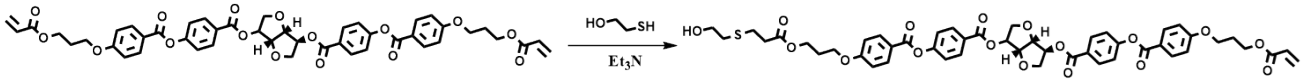
Table S4. The data of TSME test.

Samples	R_f(%)		R_r(%)		
	S0→S1	S1→S2	S2→S1	S1→S0	S2→S0
$RM_{0.5\%}$-$CLCE_{5\%}$	72.2±0.8	99.9±0.1	84.5±0.3	99.9±0.1	99.9±0.0
$RM_{4\%}$-$CLCE_{5\%}$	49.8±0.4	99.7±0.2	95.5±0.2	99.5±0.3	99.8±0.0
$RM_{8\%}$-$CLCE_{5\%}$	39.7±0.7	99.2±0.2	97.6±0.5	97.8±0.6	99.6±0.1

Table S5. The results of 2W-SME test under constant stress.

Samples	$\mathcal{E}_i$(%)	R_{act}(%)	R_{rec}(%)
$RM_{0.5\%}$-$CLCE_{5\%}$	7.5	36.0±0.2	99.9±0.1
$RM_{4\%}$-$CLCE_{5\%}$	7.3	30.9±0.1	99.9±0.1
$RM_{8\%}$-$CLCE_{5\%}$	7.4	25.6±0.2	99.5±0.1

Supporting Scheme and Figures:



Scheme S1. Synthetic route of the mDK756.

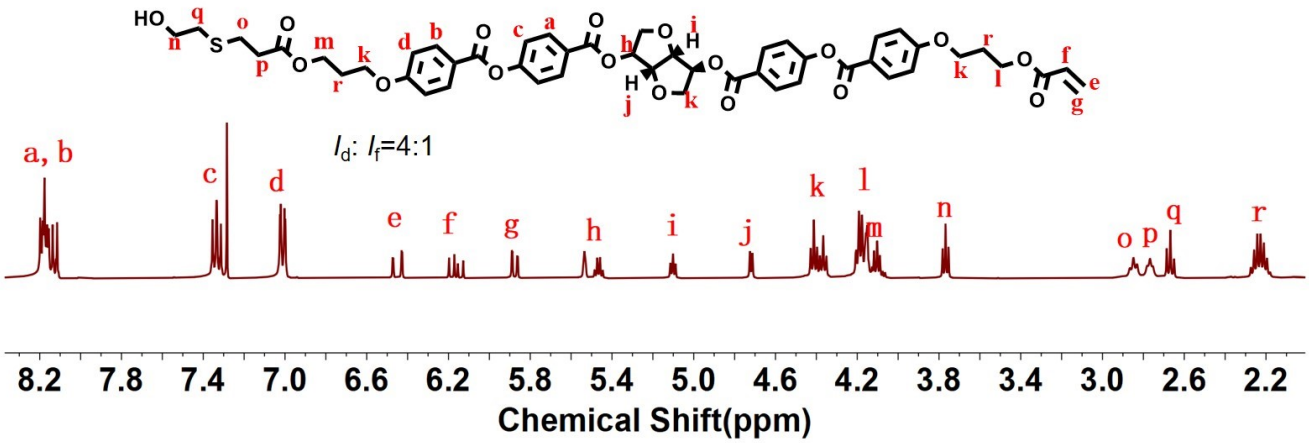


Fig. S1 ^{1}H NMR spectrum of mDK756.

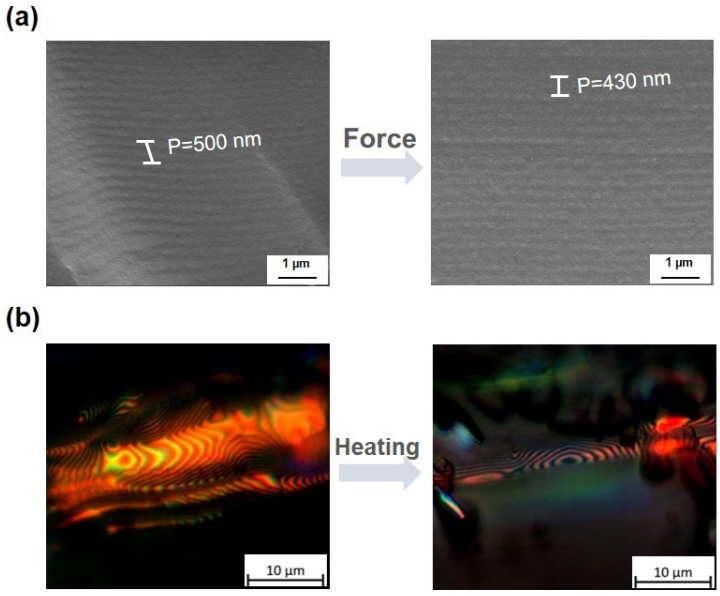


Fig. S2 Helical structure characterizations of the CLCE under stretching and heating conditions.

a) SEM image of $RM_{4\%}$-$CLCE_{3.8\%}$ with the pitch indicated in it, b) POM image of $RM_{4\%}$-$CLCE_{3.8\%}$ film in reflection mode.

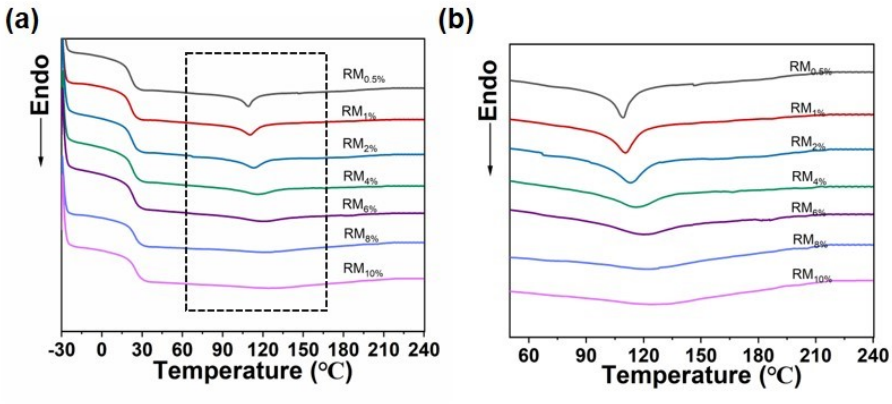


Fig. S3 DSC curves of CLCEs. a) The second heating process, b) A partial enlargement of the part circled in (a). Rates: 10 °C/min.

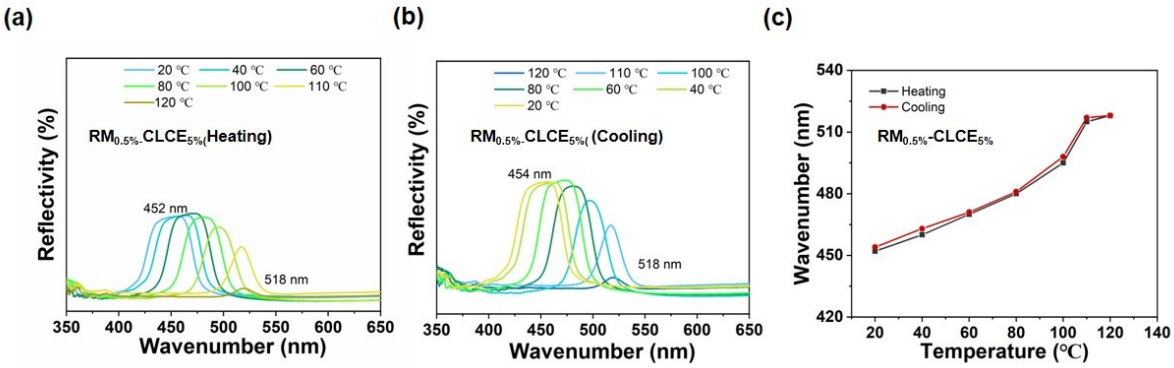


Fig. S4 Reflectance spectra of $RM_{0.5\%}$-$CLCE_{5\%}$ film at different temperatures during heating (a) and cooling process (b), and the λ_C *vs*. *T* plots (c).

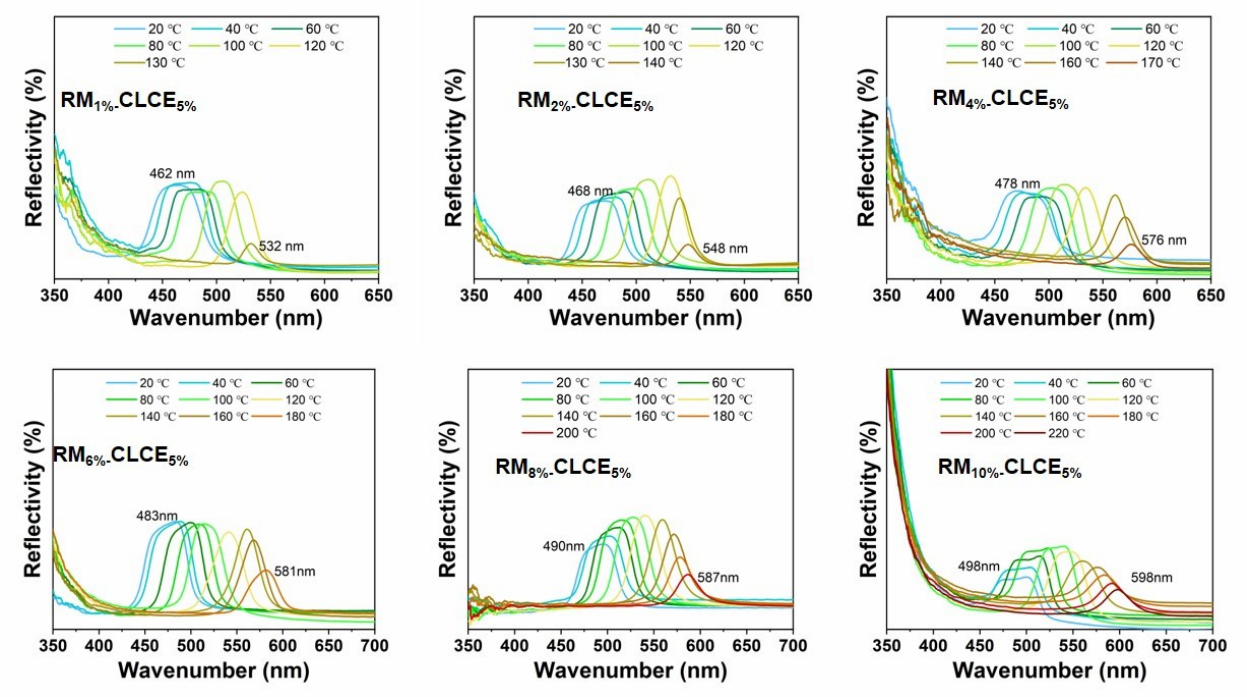


Fig. S5 Reflectance spectra of RM_x-$CLCE_{5\%}$ films upon heating from 20 °C to respective maximum color-change temperature (T_{max}).

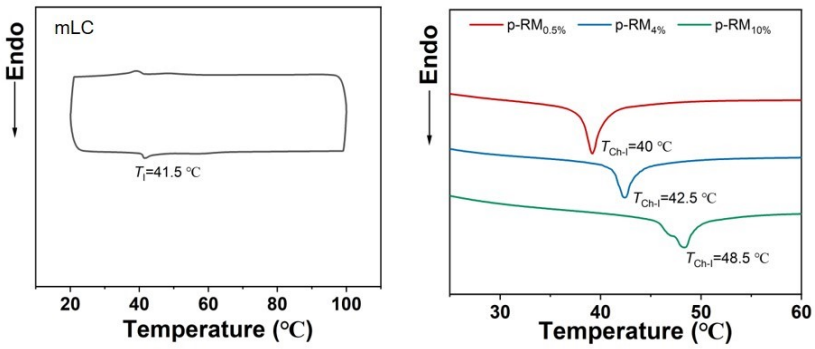


Fig. S6 DSC curves of mLC and p-RM_x (x=0.5%, 4%, 10%) CLC precursors.

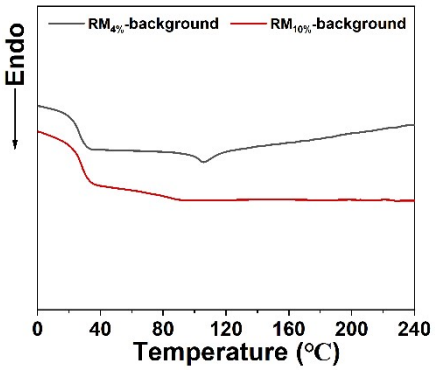


Fig. S7 DSC curves of backgrounds of the "Flowers" created form $RM_{4\%}$-$CLCE_{5.5\%}$ and $RM_{10\%}$-$CLCE_{6\%}$.

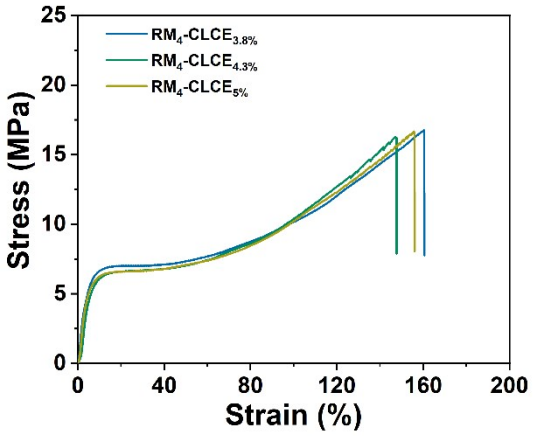


Fig. S8 Stress–strain curves of $RM_{4\%}$-$CLCE_y$ (y=3.8, 4.3 and 5%) films.

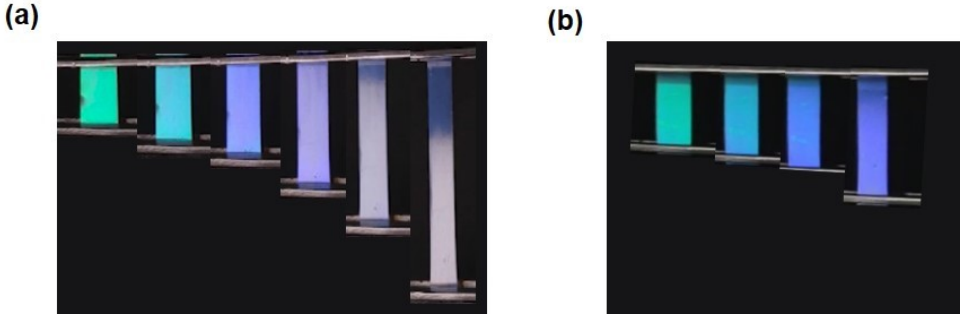


Fig. S9 Photographs of $RM_{0.5\%}$-$CLCE_{4.3\%}$ (a) and $RM_{10\%}$-$CLCE_{5\%}$ (b) under applied tensile strain before fracture.

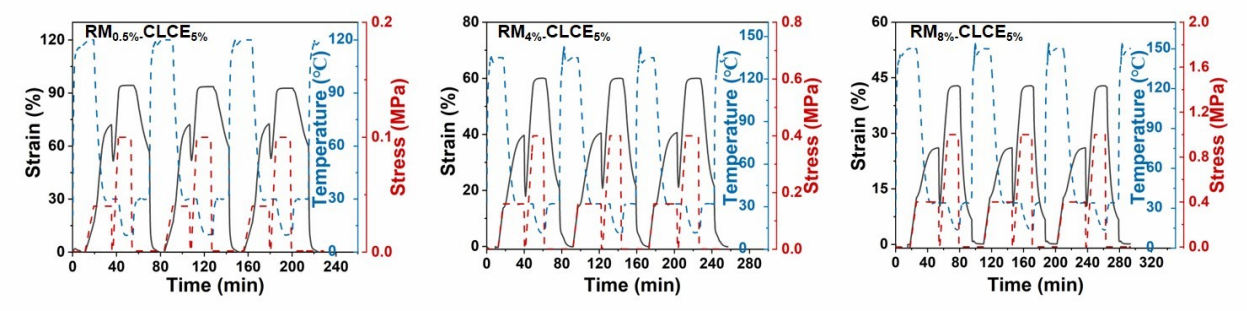


Fig. S10 Triple-SME test in thermomechanical analysis of CLCEs recorded by DMA.

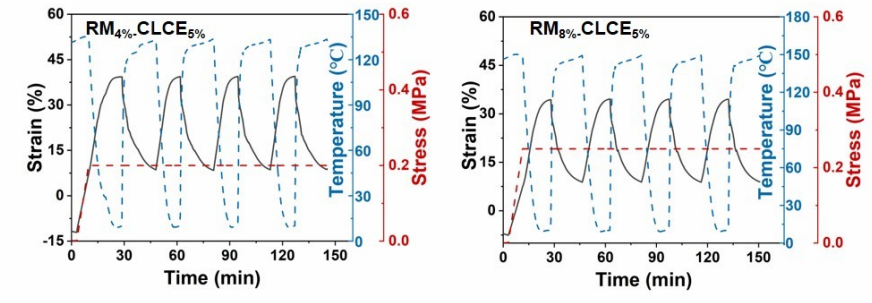


Fig. S11 The results of the 2W-SMEs of $RM_{4\%}$-$CLCE_{5\%}$ and $RM_{8\%}$-$CLCE_{5\%}$ recorded by DMA.

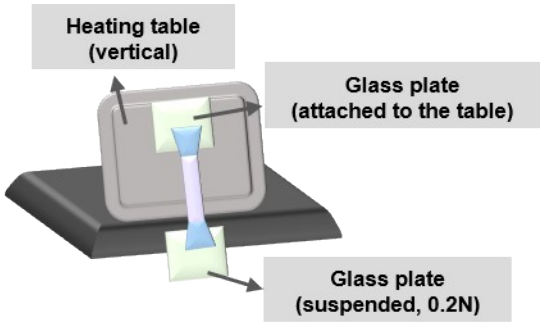


Fig. S12 The device showing 2W-SME under constant stress. It concludes a heating table, two glass plates and the CLCE film. Firstly, ends of the film are pasted on the two glass plates, and one of the glass plates is fixed on the heating table and the other is suspended. Initially, there is support under the bottom glass plate to ensure that the film has no initial strain. Then, the support is removed when turning on the heating table and temperature increasing to 125 °C, and the film is applied constant stress (the gravity generated by the glass plate). Next, turning off the heating

table, the device cools to 10 °C (room temperature during experimental operation), which ensures sufficient arrangements of mesogens during cooling to obtain remarkable excitation strain. Finally, reheating to 125 °C, the film undergoes contraction. Meanwhile, the entire process of 2W-SME involves both temperature changes and variations in strain, so color changes during the entire processes.

Fig. S13 Heat-induced peeling. A strip of our LCE ($RM_{0.5\%}$-$CLCE_{3.5\%}$, width: w = 7.5 mm, thickness: d = 0.32 mm, and length of ~25 mm) was first adhered on a glass slide where the LCE was in the chiral phase. Then, one side of the strip is pulled at 90° from the substrate under a constant force of 0.2 N, by hanging a weight. The sample was then heated beyond $T_{Ch\text{-}I}$ from the top side, and the debonding and peeling was observed.

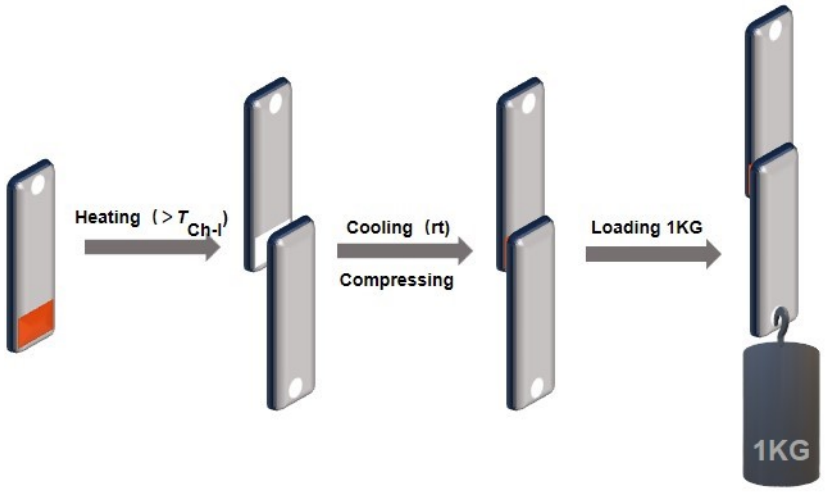


Fig. S14 Schematic diagram of adhesion process.

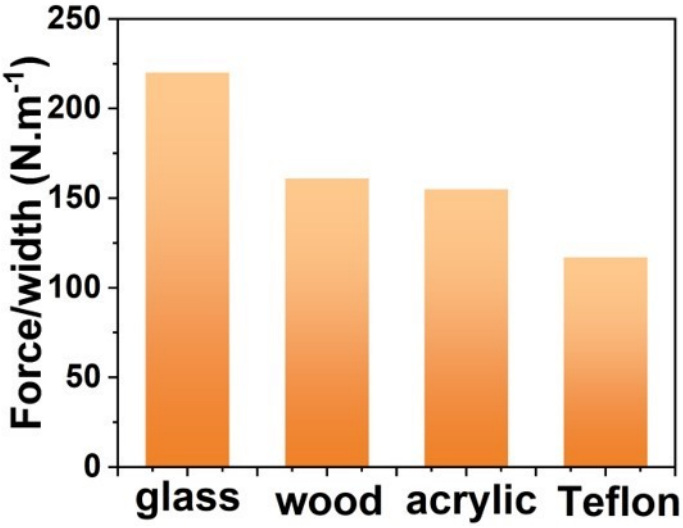


Fig. S15 Peeling strength of $RM_{0.5\%}$-$CLCE_{3.5\%}$ on various substrates.

Movie S1. The color changes of purple "Flower" ($RM_{10\%}$-$CLCE^{5.5\%}$) upon heating.

Movie S2. The color changes of light-purple "Flower" ($RM_{4\%}$-$CLCE^{6\%}$) upon heating.

Movie S3. The color changes of CLCE film ($RM_{4\%}$-$CLCE^{3.8\%}$) upon mechanical stretching.

Movie S4. The deformation and color changes of the CLCE film ($RM_{4\%}$-$CLCE^{3.8\%}$) when lifting 1 kg and 2 kg weight dumbbells.

Movie S5. The temperature-dependent adhesion analysis of the CLCE film ($RM_{0.5\%}$-$CLCE^{3.5\%}$) where Teflon, wood and glass plates were adhered to the CLCE on the tip of the bar from a box, and were transferred to the target position, and released at 130 °C.

References

1. Z.-B. Wen, D. Liu, X.-Y. Li, C.-H. Zhu, R.-F. Shao, R. Visvanathan, N. A. Clark, K.-K. Yang and Y.-Z. Wang, *ACS Appl. Mater. Interfaces*, 2017, **9**, 24947-24954.
2. Z.-Y. Xu, L. Li, L.-Y. Shi, K.-K. Yang and Y.-Z. Wang, *Macromolecules*, 2022, **55**, 5104-5114.