Supplementary Information

Two helices from one chiral centre-self organization of disc shaped chiral nanoparticles

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Contents

1 Materials and Instrumental Methods

All reactions were conducted under nitrogen. All solvents were of AR quality and used without further purification. All chemicals were purchased from Sigma-Aldrich and used as received. Column chromatographic separations were performed on silica gel (60-120, 100-200 & 230-400 mesh). Thin layer chromatography (TLC) was performed on aluminium sheets pre-coated with silica gel (TLC Silicagel 60 F_{254}, Merck KGaA, Germany).

^{1}H-NMR was recorded at 400 MHz on a JEOL Eclipse 400 FT NMR spectrometer at ambient temperatures. All ^{1}H-NMR spectra were carried out using deuterated chloroform.

DSC data was collected on a Mettler-Toledo DSC822e in nitrogen against an indium standard.

High-resolution small-angle powder diffraction experiments were recorded on Beamlines BL16B1 at Shanghai Synchrotron Radiation Facility (SSRF). Samples were held in evacuated 1 mm capillaries. A modified Linkam hot stage with a thermal stability within 0.2 ºC was used, with a hole for the capillary drilled through the silver heating block and mica windows attached to it on each side. q calibration and linearization were verified using several orders of layer reflections from silver behemate and a series of n-alkanes. A Pilatus detector was used for SAXS.

Mesophase behaviour of the samples was carried out using an Olympus BX51 polarising microscope. The microscope was equipped with a Mettler-Toledo FP900 heating stage.

UV/Vis spectra were recorded on Lambda 25 (Perkin-Elmer).

Circular dichroism (CD) spectroscopy experiments were performed at beamline B23 of the Diamond Light Source. An intense synchrotron-generated light beam of 0.8 x 1.5 mm^2 in diameter was used in the spectrometer, with the ability of samples to be scanned in xy plane and rotated. The beam was deflected vertically through the sample held horizontally between two quartz glass windows in a Linkam hot stage. The CD cells were made by constructing a sandwich structure with monomer or AuDLC* nanocomposite positioned between an untreated quartz glass plates. To better detect whether there is any local structural twist occurring in the mesophase, the sample AuDLC* was sheared manually in the preparation of the quartz cell before the CD experiments to cancel the birefringence.

TEM were conducted by a JEOL 2010 high resolution with EDS capability and a Gatan Ultrascan 4000 camera for excellent image quality.

2 Synthesis of Chiral Discogen

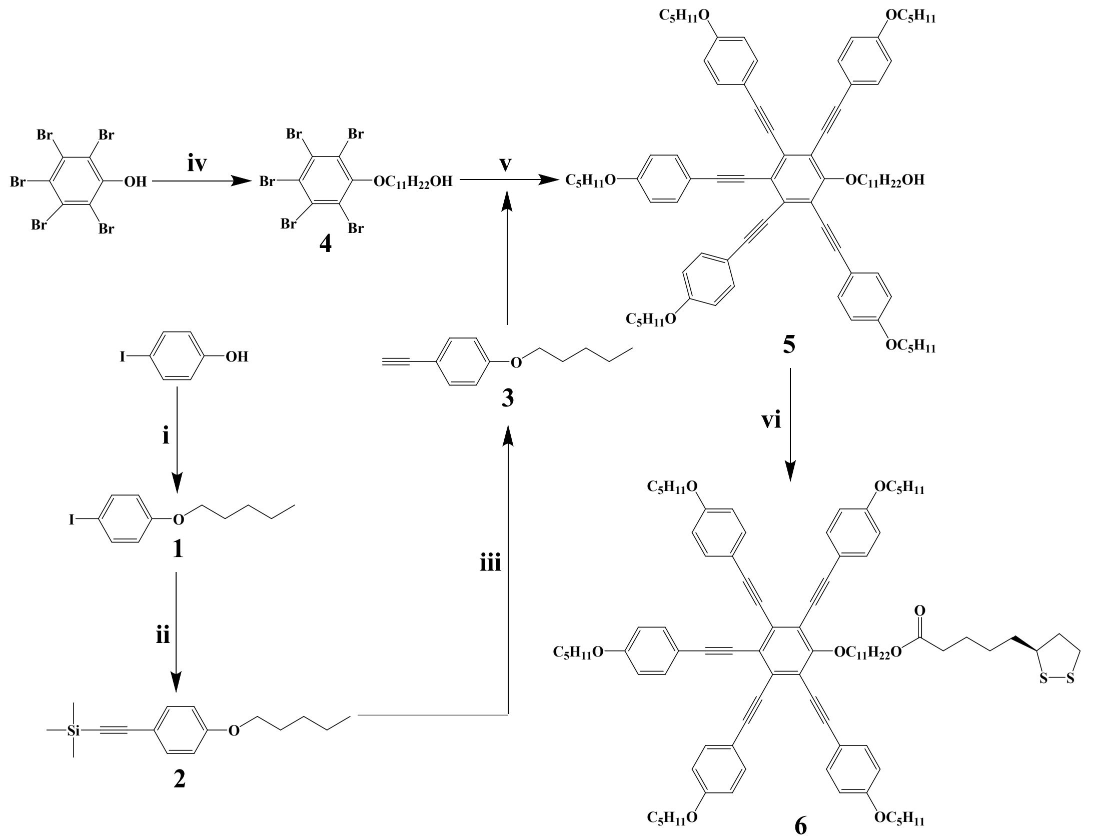


Fig. S1 Synthetic route of chiral discogen. (i) 1-Bromopentane/K_2CO_3/Butanone/95 ℃. (ii) TMSA/CuI/NEt_3/$Pd(PPh_3)_2Cl_2$/RT. (iii) KF/DMF/H_2O/RT. (iv) 11-Bromo-1-undecanol/K_2CO_3/Butanone/N_2/95 ℃. (v) PPh_3/NEt_3/$Pd(PPh_3)_2Cl_2$/LiBr/CuI/THF/N_2/102 ℃. (vi) (R)-(+)-1, 2-Dithiolane-3-pentanoic acid/DMAP/DIC/DCM/N_2/RT.

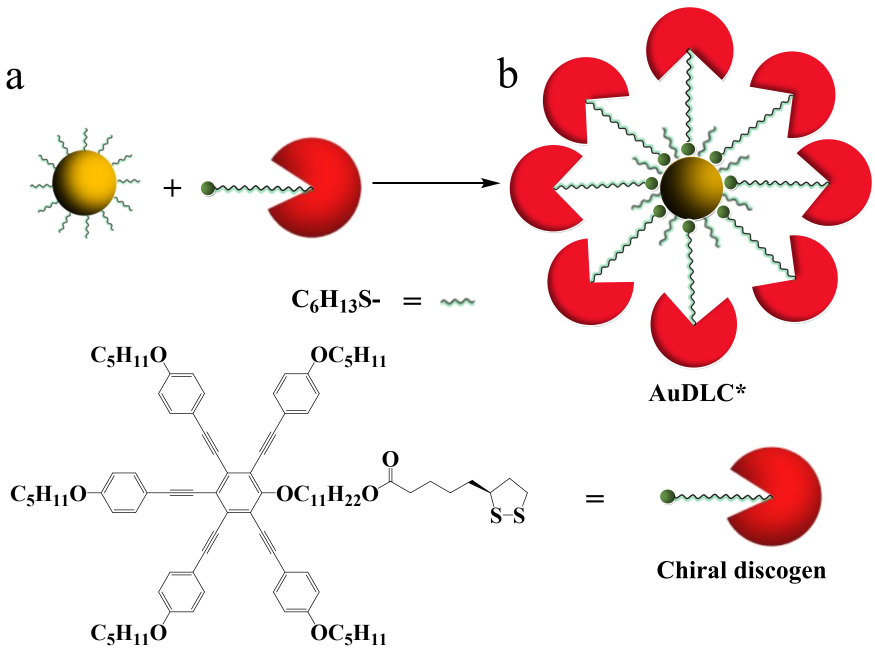
Precursor discogen[1] **5** (100.0 mg, 0.09 mmol), (R)-(+)-1, 2-Dithiolane-3-pentanoic acid (65.0 mg, 0.32 mmol) and DMAP (37.0 mg, 0.30 mmol) were dissolved in dry DCM (15 ml). The mixture was deoxygenated with bubbling nitrogen for 1 hour. Then DIC (0.16 ml, 1.00 mmol) was added in one portion and it was stirred at RT under nitrogen atmosphere for 3 days. The solvent was evaporated and the product was purified by column chromatography (hexane/ethyl acetate 4:1) to obtain the first spot on the TLC plate. After recrystallization in hexane, yellow crystals **6** was obtained (0.11 g, 93.1%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 0.91 (t, 15H, CH_3), 1.20-1.51 (m, 36H, CH_2), 1.51-

1.93 (m, 20H, $OCH_2C\underline{H}_2$), 2.29 (t, 2H, CH_2CO), 2.39-2.49 (m, 1H, CH), 3.10 (m, 2H, CH_2S), 3.50-3.60 (m, 2H, CH_2S), 3.97 (t, 10H, OCH_2), 4.03 (t, 2H, Ar-OCH_2), 4.32 (t, 2H, CH_2OOC), 6.82-6.90 (m, 10H, CH_{arom}), 7.47-7.55 (m, 10H, CH_{arom}).

^{13}C-NMR (400 MHz, $CDCl_3$): δ = 14.12, 22.56, 28.27, 28.74, 28.86, 28.98, 29.63, 34.21, 38.56, 64.63, 68.17, 76.78, 77.10, 77.41, 114.66, 115.42, 133.19, 133.36, 159.70. Mass spectrometry (MS): *m/z* (CI) 1400.80 ($M+NH_4^+$, 100%); HRMS Found: 1400.7968 $C_{90}H_{110}O_8S_2NH_4$ ($M+NH_4^+$) Requires 1400.7980.

3 Synthesis of AuDLC*



Scheme 1 Schematic representations of (a) (left) 1-Hexanethiol capped AuNPs and (b) (right) Exchange reaction yielding AuDLC*. Bottom: Chemical structure of the groups covering the particle surface (1-hexanethiol and chiral discogen).

4 POM of Chiral Discogen

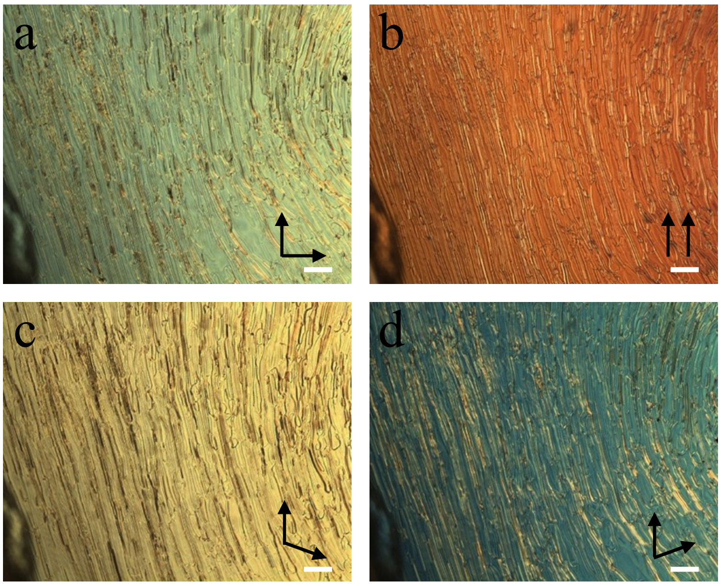


Fig. S2 POM micrographs (x 50 μm) of chiral discogen at (a) 75.2 ℃ (90° crossed polarizer). (b) 75.2 ℃ (0° crossed polarizer). (c) 75.2 ℃ (110° crossed polarizer). (d) 75.2 ℃ (70° crossed polarizer).

5 DSC of Chiral Discogen

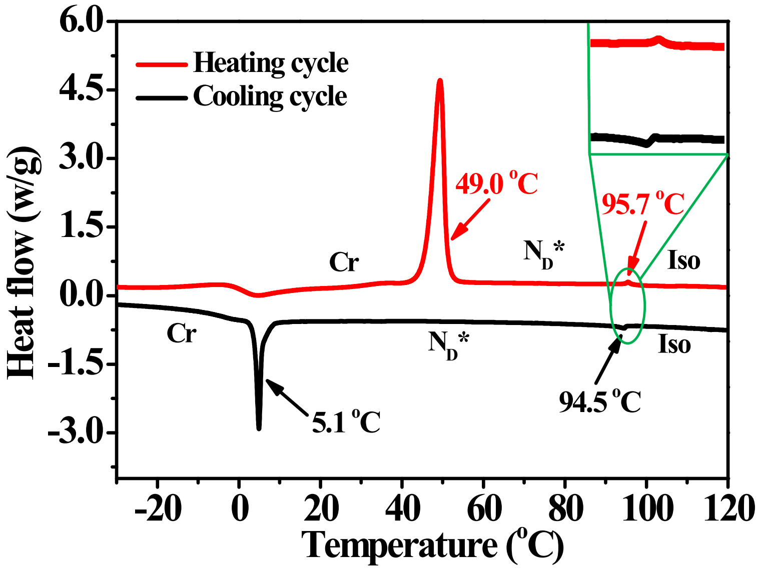


Fig. S3 DSC results of chiral discogen at a heating and cooling rate of 10.0 ℃ /min.

6 [1]H-NMR of AuDLC* and Chiral Discogen

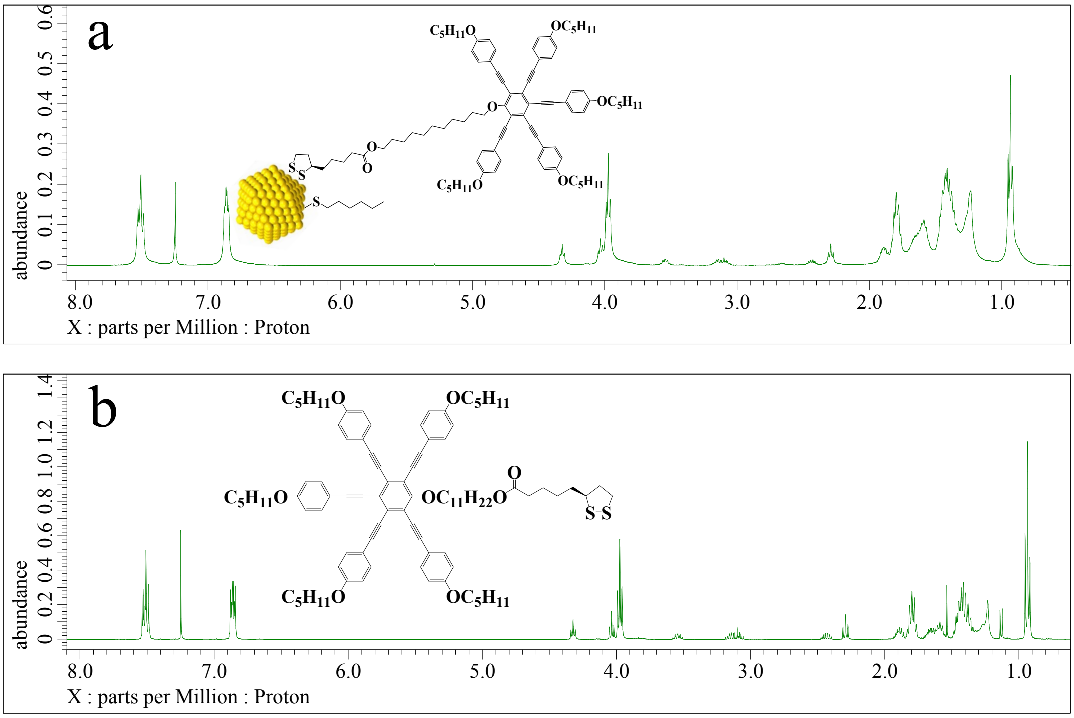


Fig. S4 ^{1}H-NMR spectra of (a) AuDLC* and (b) Chiral discogen.

7 Calculations of the Number of Ligands on NPs and TEM Photo of Thiol-capped AuNPs

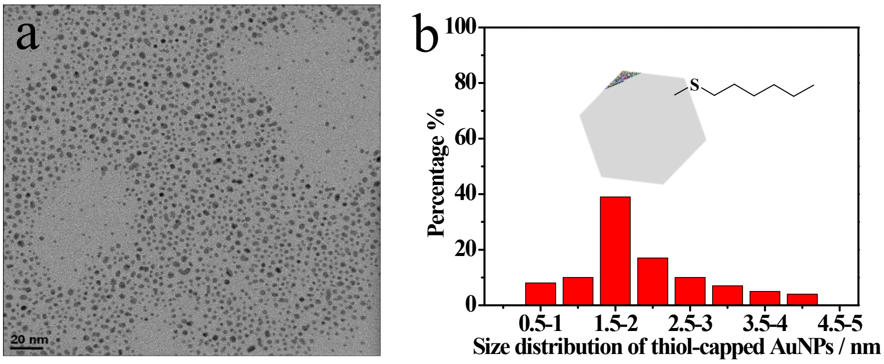


Fig. S5 (a) High-resolution TEM image of 1.9 nm 1-hexanethiol capped AuNPs. (b) The size distribution of 1-hexanethiol capped AuNPs.

The number of Au atoms in one single AuNPs is determined based on the formula:

$$N_{Au} = \frac{4 \times \pi \times R^3}{3 \times v_g} = \frac{4 \times \pi \times D^3}{8 \times 51}$$

R-radius of AuNPs (Å); *D*-diameter of AuNPs (Å); *vg*-volume of gold atom (v_g = 17 Å); 1 Å = 0.1 nm.

Based on TEM picture in Figure S5a, the average diameter of Au core is 1.9 nm.

$$N_{Au} = \frac{4 \times \pi \times 19^3}{8 \times 51} = 211$$

So, the number of gold atoms per particle is $N_{Au/particle}$ = 211.

According to the model developed by Gelbart et al[2], the number of total ligands on gold surface is obtained by the formula:

$$N_{Lig} = \frac{4 \times \pi \times R^2}{21.4} = \frac{\pi \times D^2}{21.4} = 53$$

In the ^{1}H-NMR spectra of AuDLC* (see Fig. S4a), the signals at δ = 7.50 ppm (CH_{arom}), δ = 6.85 ppm (CH_{arom}), δ = 0.92 ppm ($-CH_3-$) can be used to estimate the molar ratio of chiral discogen and 1-hexanethiol ($Int_{\delta = 7.50}$: $Int_{\delta = 6.85}$: $Int_{\delta = 0.92}$ = 9.92 : 10.00 : 16.98). The molar ratio of chiral discogen and 1-hexanethiol is 3 : 2. Combined with the number of thiol per particle 53, there are 32 chiral discogen and 21 1-hexanethiol on per NP.

The molecular weight of total number of gold atoms is 41567.6;

The molecular weight of total ligands on per NP is 46680.6

The molecular weight of per particle is 88248.2.

8 TGA of AuDLC*

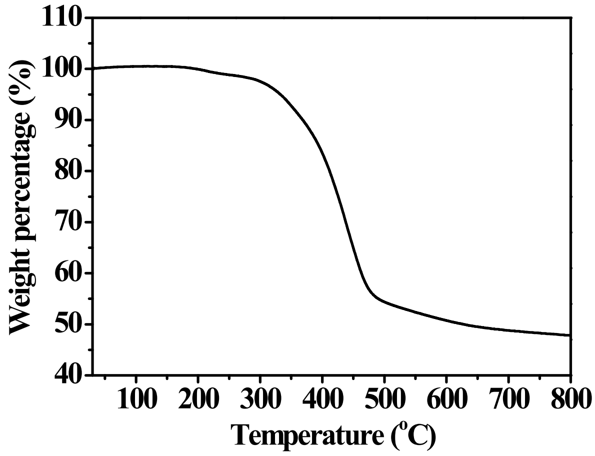


Fig. S6 TGA result of AuDLC* (the weight fraction of gold in AuDLC* is about 47.85 wt%). In the former calculation, the weight fraction of gold in AuDLC* is 47.10 wt%, very close to the TGA result.

Table S1 Calculation of ligands and TGA results for AuDLC*.

Input of small sized AuNPs	
Average size from TEM for Au core	1.9 nm
Number of gold atom per particle	211
Number of total ligands on Au surface	53
M.Wt. of total number of Au atoms	41567.6 g mol^{-1}
Calculated ligands on AuDLC*	
Chiral discogen	32
1-Hexanethiol	21
M.Wt. of total ligands on Au surface	46680.6 g mol^{-1}
Molecular weight of particles	88248.2 g mol^{-1}
TGA results of AuDLC*	
Gold left in TGA data	47.85 wt%
Gold left in calculation above	47.10 wt%

9 UV-Vis Spectra of the AuDLC* Nanocomposite

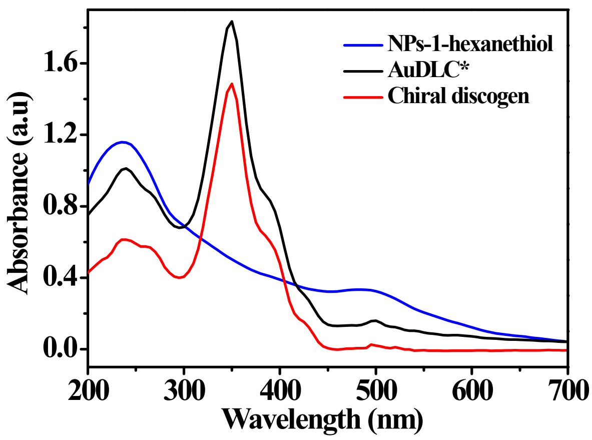


Fig. S7 UV-Vis spectra of 1-hexanethiol capped AuNPs, AuDLC* and chiral discogen (0.01 mol L^{-1} in DCM).

10 POM of AuDLC*

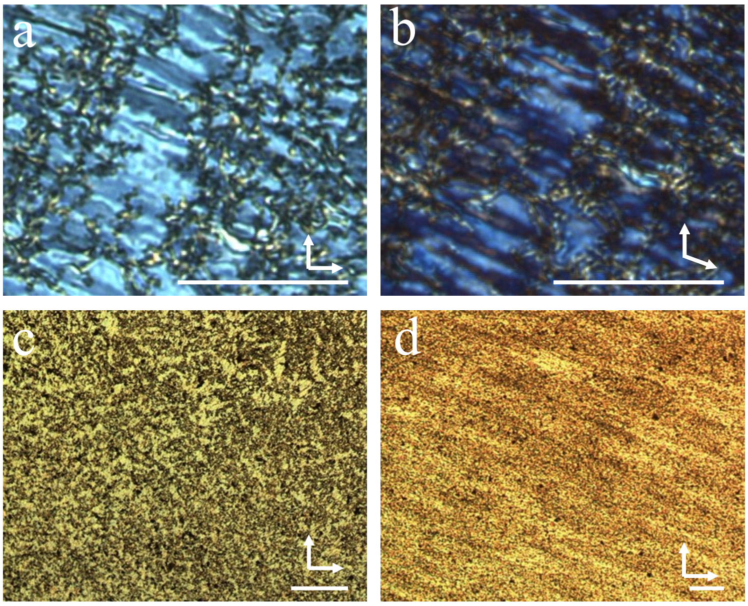


Fig. S8 POM micrographs of AuDLC* (a) 79.0 ℃ (90º crossed polarizer) (x 25 μm). (b) 79.0 ℃ (110º crossed polarizer) (x 25 μm). (c) 63.5 ℃ (90º crossed polarizer) (x 100 μm). (d) 37.8 ℃ after gently pressing (90º crossed polarizer) (x 100 μm).

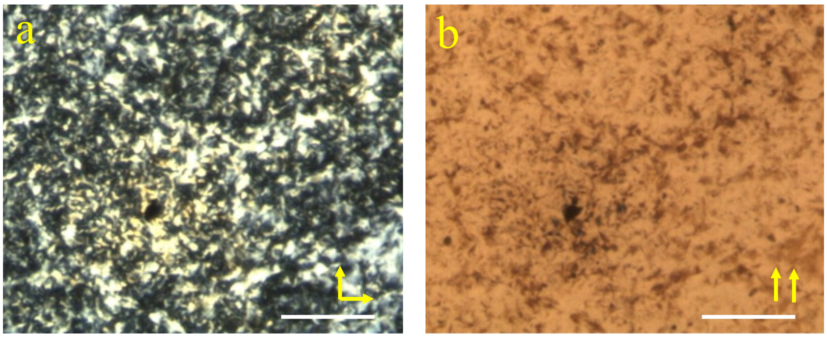


Fig. S9 POM micrographs (x 25 μm) of AuDLC* on the edge of slide at RT after several days cooling (a) 90° crossed polarizer and (b) 0° crossed polarizer.

11 Synchrotron XRD Results of AuDLC*

Table S2 Experimental and calculated *d*-spacing, relative integrated intensities for the columnar phase with *p*2 symmetry at 100 ℃. All intensities values are Lorentz and multiplicity corrected. The unit cell parameters: a = 4.17 nm, b = 2.52 nm, γ = 48.4°.

(*hk*)	*q*	d_{exp}	d_{cal}
(10)	2.0160	3.12	3.12
(01)	3.3289	1.89	1.89
(1$\bar{1}$)	4.9051	1.28	1.28

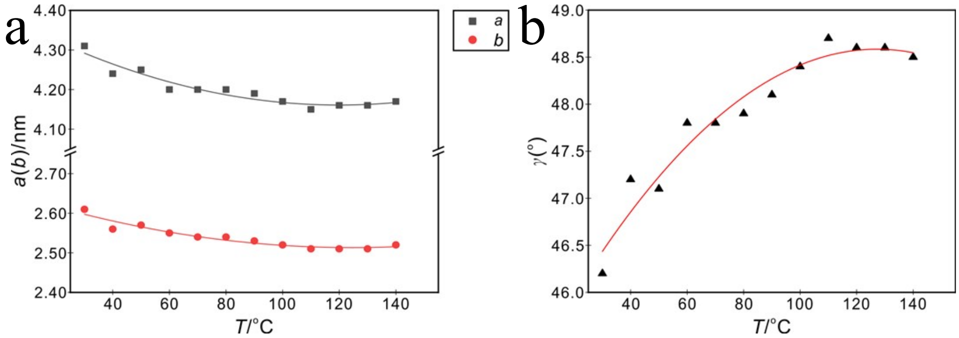


Fig. S10 The diagrams of lattice parameters versus temperature.

Table S3 Calculation of volume from XRD results for AuDLC*.

Input		
density Au	19.32	g cm^{-3}
density organic fraction	1.26	g cm^{-3}
weight fraction of gold (from TGA, Figure S6)	47.85	%
a	4.17	nm
b	2.52	nm
γ	48.4	deg
Calculated		
unit cell area (A)	10.51	nm^2
m_{Au}/m_{org}	91	%
V_{Au}/V_{org}	5.93	%
$V_{particle}$	3.60	nm^3
unit cell volume (Ac)	64.30	nm^3
spatial direction c not defined by the lattice	6.12	nm
estimated maximum possible extension of overall system (single NP)	8.70	nm

12 Circular Dichroism Spectra of Monomer and AuDLC*

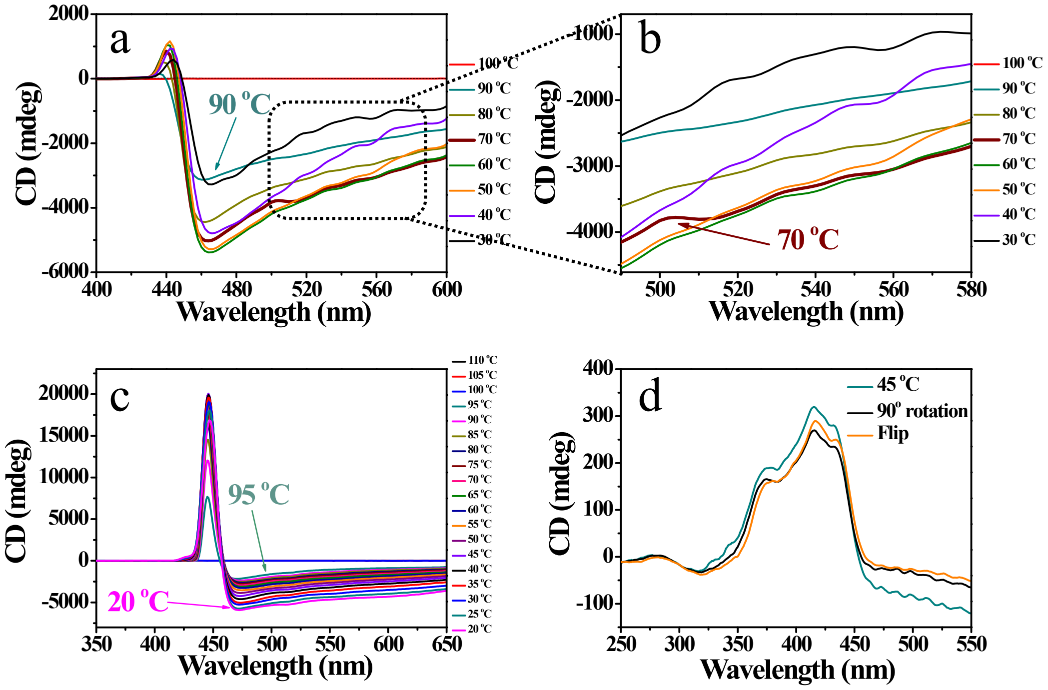


Fig. S11 SRCD spectra of (a) AuDLC* in thin film recorded every 10 °C upon cooling from 100 °C to 30 °C. (b) The enlarged dotted region in (a). (c) Chiral discogen in thin film recorded every 5 °C upon cooling from 110 °C to 20 °C. (d) **Sheared** AuDLC* recorded at 45 °C with 90° rotation around the center of the light beam and turning the sample over (flip).

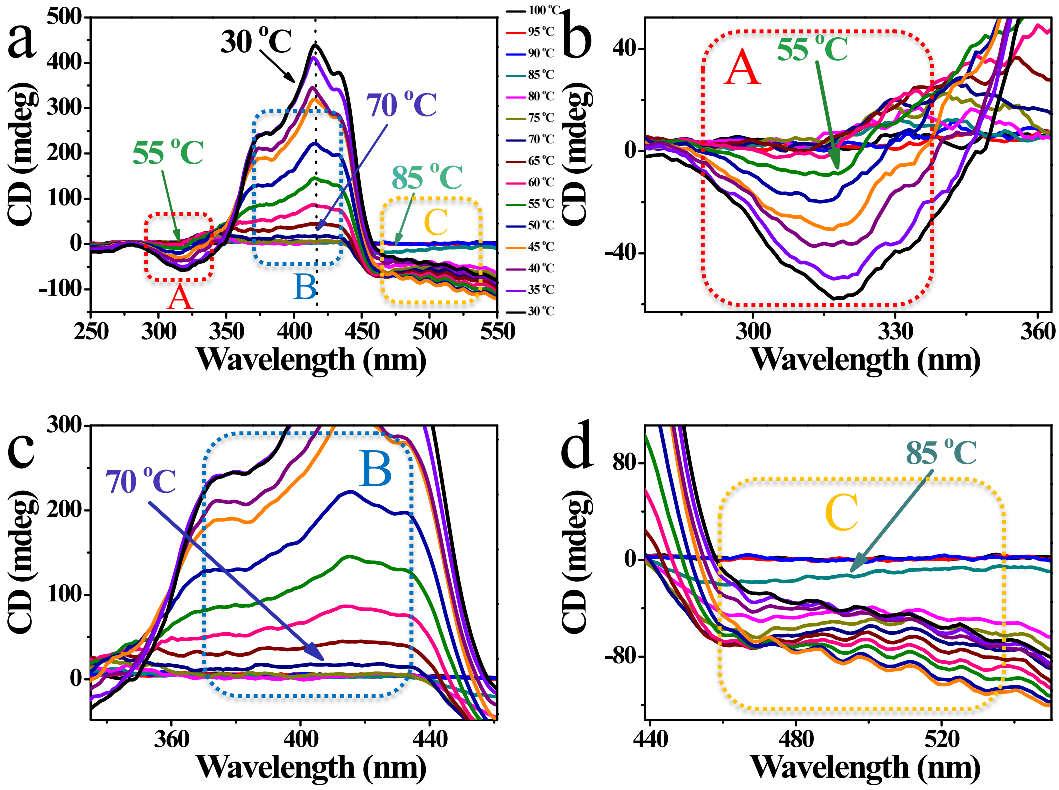


Fig. S12 SRCD spectra of (a) **Sheared** AuDLC* recorded every 5 °C upon cooling from 100 °C to 30 °C. (b) The enlarged region A in (a). (c) The enlarged region B in (a). (d) The enlarged region C in (a).

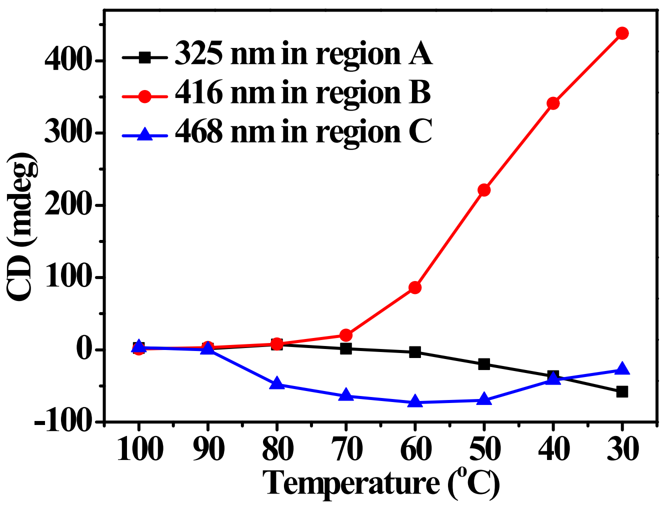


Fig. S13 The CD intensities at a selected wavelength in each region (325 nm in region A, 416 nm in region B and 468 nm in region C) from Fig. 1f and Fig. S12 are plotted as a function of temperature. These plots clearly show the difference in the formation process between the two helical structures.

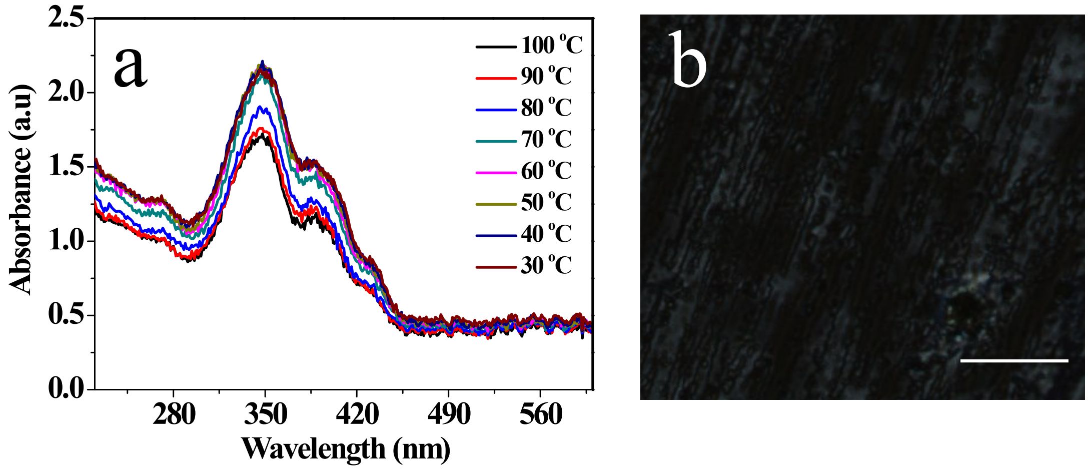


Fig. S14 (a) UV-Vis spectra of AuDLC* in thin film recorded every 10 ℃ upon cooling from 100 ℃ to 30 ℃. (b) POM micrographs (x 20 μm) of gently **sheared** AuDLC* at 45 ℃ (90° crossed polarizer).

13 Reference

(1) S. Kumar, S. K. Varshney and D. Chauhan, *Mol. Cryst. Liq. Cryst*., 2003, **396**, 241-250.

(2) D. V. Leff, P. C. Ohara, J. R. Heath and W. M. Gelbart, *J. Phys. Chem*., 1995, **99**, 7036-7041.