Supporting Information

Induction, Fixation and Recovery of Self-Organized Helical

Superstructures in Achiral Liquid Crystalline Polymer

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1. Materials and Methods

1.1 Design and synthesis of the monomers and polymers

Materials: The diisopropyl azodicarboxylate (DIAD, 98%. 3A Chemicals), triphenylphosphine (TPP, >99%, Greagent), (R)-(-)-butanol (>99.0%, TCI), (S)-(+)-2-butanol (>98.0%, TCI), (R)-(-)-octanol (>99%, TCI) and (S)-(+)-octanol (>99%, TCI) were used without further purification. 1-Chloro-6-hydroxyhexane and methacryloyl chloride were purchased from Sigma-Aldrich. 2,2-Azobisisobutyronitrile (AIBN) was recrystallized twice from ethanol. 2-Cyanoprop-2-yl-1-dithionaphthalate (CPDN) was synthesized according to the literature.¹ The monomer 4-methoxy - 4'-(2-hexyloxy methacrylate) azobenzene (Az) was obtained as reported previously.²¹H NMR (CDCl₃, 300 MHz) of the monomer Az, (δ, ppm): 7.87 (m, 4H), 7.26 (m, 2H), 6.99 (m, 2H), 6.10 (d, 1H), 5.54 (d, 1H), 4.18 (t, 2H), 4.03 (t, 2H), 3.92 (s, 3H), 1.98 (s, 3H), 1.81 (m, 2H), 1.71 (m, 2H), 1.50 (m, 4H). 4-Hydroxy-4'-(2hydroxy ethoxy) azobenzene (A, Scheme S1) was synthesized according the literature.³ ¹H NMR (DMSO-*d*₆, 300 MHz) of A, (δ, ppm): 10.17 (s, 1H), 7.78 (m, 4H), 7.10 (m, 2H), 6.92 (m, 2H), 4.91 (t, 1H), 4.08 (t, 2H), 3.75 (m, 2H).



Scheme S1 Synthetic route to the chiral dopants (a), monomer AzOH (b) and polymers (c).

Synthesis of compound (R)-4-methoxy -4'-(octan-2-yloxy) azobenzene (Azo-R5)

4-Methoxy-4-hydroxyl azobenzene (500.0 mg, 2.19 mmol), (*R*)-(-)-2-octanol (284.7 mg, 2.19 mmol) and diisopropyl azodicarboxylate (0.67 mL, 3.28 mmol) were dissolved in 10 mL dried THF and cooled in a water–ice bath for 0.5 h, then the solution of triphenylphosphine (860.0 mg, 3.28 mmol) in 5 mL THF was added dropwise during 5 min. The mixture was stirred at room temperature overnight. After that, filtered off the precipitate, and removed the solvent. The solid was washed with ether for three times. After concentrating the washing liquid, the product was further purified by column chromatography with hexane/ethyl acetate (15:1 v/v) (543.5 mg, 73.0% yield). ¹H NMR (DMSO-*d*₆, 300 MHz) of the compound Azo-*R*5, (δ , ppm):

7.82 (m, 4H), 7.09 (m, 4H), 4.56 (m, 1H), 3.85 (s, 3H), 1.63 (m, 2H), 1.26 (m, 3H), 1.28 (m, 8H), 0.86 (t, 3H). The other chiral dopants with different configuration and different alkyl chain length were prepared in similar procedures.

¹H NMR (DMSO-*d*₆, 300 MHz) of the compound **Azo-S5**, (δ, ppm): 7.82 (m, 4H), 7.11 (m, 4H), 4.55 (m, 1H), 3.85 (s, 3H), 1.63 (m, 2H), 1.26 (m, 3H), 1.28 (m, 8H), 0.86 (t, 3H).

¹H NMR (DMSO-*d*₆, 300 MHz) of the compound **Azo-R1**, (δ, ppm): 7.82 (m, 4H), 7.10 (m,

4H), 4.51 (m, 1H), 3.85 (s, 3H), 1.66 (m, 2H), 1.26 (m, 3H), 0.93 (t, 3H).

¹H NMR (DMSO-*d*₆, 300 MHz) of the compound **Azo-S1**, (δ, ppm): 7.82 (m, 4H), 7.10 (m, 4H), 4.51 (m, 1H), 3.85 (s, 3H), 1.67 (m, 2H), 1.28 (m, 3H), 0.94 (t, 3H).

Synthesis of 4-(2-hydroxy ethoxy)-4'-(2-hexyloxy methacrylate) azobenzene (AzOH)

6-Chlorohexyl methacrylate (B) was synthesized via the following steps. A solution of 6chlorohexanol (5.0 g, 36.6 mmol), triethylamine (12 mL, 86.3 mmol) in dried THF (100 mL) was stirred at 0 °C for 0.5 h. Then the methacryloyl chloride (7.6 g, 73.1 mmol, dissolved in 20 mL THF) was added dropwise to the mixture. After 30 min of stirring at 0 °C, the reaction liquid was kept at 30 °C for 12 h. Then the filtrate was collected by filtration and washed with saturated NaHCO₃ solution. The product was afforded after the removal of the solvent and further purified through column chromatography using pure hexane as eluent (6.02 g, 80.6% yield). ¹H NMR (CDCl₃, 300 MHz) of B: 6.09 (d, 1H), 5.55 (d, 1H), 4.15 (t, 2H), 3.53 (t, 2H), 3.92 (s, 3H), 1.94 (s, 3H), 1.74 (m, 4H), 1.47 (m, 4H).

The monomer AzOH was synthesized via the following steps. The compound A (3.0 g, 11.6 mmol), potassium carbonate (6.4 g, 46.5 mmol), a small amount of potassium iodide and 35 mL DMF were added into a 250 mL round bottom flask. The reaction mixture was refluxed under argon at 80 °C for 1 h. After that a solution of B (3.21 g, 15.7 mmol) in 15 mL DMF was then added dropwise to the above mixture. Then the reaction was carried out at 80 °C for 12 h. Finally, the reaction mixture was cooled down to room temperature and then poured into 200 mL water. The product was collected by filtration and further purified by column

chromatography with hexane/ethyl acetate (5:1 v/v) (3.62 g, 73.3% yield). ¹H NMR (DMSOd₆, 300 MHz) of the monomer AzOH, (δ, ppm): 7.82 (m, 4H), 7.10 (m, 4H), 6.02 (d, 1H), 5.66 (d, 1H), 4.92 (t, 1H), 4.09 (m, 6H), 3.75 (m, 2H), 1.87 (s, 3H), 1.76 (m, 2H), 1.66 (m, 2H), 1.44 (m, 4H).

Synthesis of the Azo-containing homopolymer (PAz) and copolymer (PAz-r-AzOH)

The side-chain Azo polymers (Scheme S1b) were synthesized by reversible addition fragmentation chain transfer (RAFT) polymerization, where CPDN and AIBN were used as the RAFT agent and the initiator, respectively. For the homopolymer PAz, the monomer Az (396 mg, 1.0 mmol), CPDN (8.35 mg, 0.03 mmol), AIBN (1.64 mg, 0.01 mmol) and dried anisole (1.5 mL) were added into a 5 mL ampoule bottle. The polymerization ratio is 100/3/1 ([monomer]₀/[CPDN]₀/[AIBN]₀). The reaction tube was flame-sealed under an argon atmosphere after deoxygenated with three freeze-thaw cycles. Then the polymerization was carried out at 70 °C for 3 h. After that, the reaction mixture was diluted with THF (2 mL) and precipitated into an excess of methanol (80 mL) twice. The polymer solid was collected by filtration and then dried in a vacuum oven overnight at 30 °C. Copolymer PAz-*r*-AzOH was obtained via the similar process, except for the polymerization ratio of the monomers. The molecular weights and hydroxyl content were calculated from the ¹H NMR spectra and GPC curves (Table S1, Fig. S4, S5).

1.2 Characterization

¹H NMR spectra were recorded on a Bruker nuclear magnetic resonance instrument (300 MHz, Brucker, Kalsruhe, Germany) using CDCl₃ and DMSO- d_6 as solvent and tetramethylsilane (TMS) as the internal standard at different temperature.

Gel-permeation chromatograph (GPC) measurements were conducted on the TOSOH HLC-8320 gel permeation chromatogragh (GPC), equipped with refractive-index and UV detectors using two TSKgel SuperMultiporeHZ-N (4.6×150 mm, 3.0μ m beads size) columns arranged in series. Polymers can be separated in the molecular weight range of 500-190k Da. DMF was used as the eluent with a flow rate of 0.35 mL/min at 40 °C. The number average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of sample was calculated with polystyrene (PS) standards.

The CD spectra were recorded on a JASCO J-1500 spectropolarimeter equipped with a Peltier-controlled housing unit using a SQ-grade cuvette, a single accumulation, a bandwidth of 2 nm, a scanning rate of 200 nm min⁻¹, a path length of 10 mm, and a response time of 1 s. The magnitude of the circular polarization at the ground state is defined as $g_{CD} = 2 \times (\varepsilon_L - \varepsilon_R)/(\varepsilon_L + \varepsilon_R)$, where ε_L and ε_R denote the extinction coefficients for left and right circularly polarized light, respectively. Experimentally, g_{CD} value is defined as $\Delta \varepsilon/\varepsilon =$ [ellipticity/32 980]/absorbance at the CD extremum.

The UV-vis spectra were recorded on a UV-2600 spectrophotometer (Shimadzu (Nakagyo-ku, Kyoto, Japan)).

The phase transition of the polymers was measured with a TA-Q100 DSC instrument. The temperature range is 20 °C to 200 °C with the first heating-cooling speed of 20 °C/min and second heating speed of 10 °C.

LC textures and birefringence of the samples were examined under a POM (Olympus Corporation, BX51-P) equipped with a hot stage (Linkam THMS600).

SAXS experiments were performed with a high-flux X-ray instrument (SAXSess mc², Anton Paar) equipped with a line collimation system and a 2200 W sealed-tube X-ray generator (CuK α , $\lambda = 0.154$ nm). The polymer samples were wrapped in aluminum foils and sandwiched in a steel sample holder.

X-ray diffraction (XRD) measurements of the samples were recorded by CuK α (λ = 0.154 nm) radiation monochromatized with a Bruker D8 ADVANCE X-ray diffractometer (Bruker, Germany).

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Difference in binding energy of polymer films was measured using X-ray photoelectron spectroscopy (XPS) (Thermo Fisher Scientific ESCALAB 250XI, A1 KR source)

1.3 Experimental methods

Preparation of the chiral polymer films. The chiral polymer films for CD measurements with thickness in the range of 100-200 nm were prepared by spin coating the polymer solution (doped with chiral Azo molecules, 12 mg/mL in THF) onto a clean quartz plate at a speed of 0.5 rpm for 6 seconds and then a speed of 1.9 rpm for 20 seconds. After dried under vacuum to remove THF, the film was heated to the nematic temperature to make sure the occurrence of chiral transmission.

Removal of chiral dopants. The polymer film containing chiral dopant was immersed in methanol for 60 h, during which the soaking solution was changed for five times. After that, the residual contents of chiral dopant in the soaking solution and polymer films were measured by ¹H NMR spectra (Fig. S12).

The storage of the supramolecular chirality. The hydroxyl-containing polymer films after chiral induction and removal of chiral dopants were placed in the top of a larger beaker in which two small beakers with 30% formaldehyde aqueous and 6 N hydrochloric acid solution were placed in separately. Then the cross-linking of the polymer chains was carried out when exposed to HCl and HCHO vapor at 25 °C for 20 h. The cross-linked polymer films were washed with pure water and dried in the vacuum at 35 °C for 12 h.

Photoisomerization process of polymer films. Photoisomerization of Azo-containing chiral polymer film was conducted with a 500 W high-pressure mercury lamp (Tokyo, Japan), Optiplex SX-UID and 502HUV) equipped with a narrow bandpass filter for the wavelength of 365 nm. The irradiation intensity was 2.5 mW cm⁻².

1.4 Structure information of the molecules and polymers

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Fig. S1 ¹H NMR spectra of the chiral dopants Azo-R5(a), Azo-S5(b), Azo-R1(c) and Azo-S1(d).



Fig. S2 HPLC spectra of the chiral dopants Azo-R5(a), Azo-S5(b), Azo-R1(c) and Azo-S1(d).



Fig. S3 ¹H NMR spectrum of the compounds A (a), B (b) and Azo monomers Az (c), AzOH (d).



Fig. S4 ¹H NMR spectrum of the polymer PAz (a) and PAz-*r*-AzOH (b).

Table S1 Molecule weight characteristics of the polymers.								
Polymer	Ratio ^a	Conv. ^b (%)	Monomer-ratio ^c (Az : AzOH)	$\mathrm{DP}_{(\mathrm{x},\mathrm{y})}^d$	$M_{n(GPC)}^{e}$ (g mol ⁻¹)	$M_{ m w}/M_{ m n}^f$		
PAz	100:0:3:1	58.2	1:0	x = 23	8100	1.12		
PAz-r-AzOH	50:50:3:1	55.7	1:0.67	x = 12, y = 8	9200	1.27		

^{*a*} Polymerization ratio: $[Az]_0/[AzOH]_0/[CPDN]_0/[AIBN]_0$. ^{*b*} Determined gravimetrically. ^{*c*}, ^{*d*} Calculated from ¹H NMR spertrum. ^{*c*} Az : AzOH (in polymer chain) = 1 : (32 / (I(b) – 4 × I(c))). ^{*d*} DP = I(b) / (4 × I(a)). ^{*e*, *f*} Determined by GPC according to PS standards in DMF.

2. Supporting Figures



Fig. S6 POM images of the PAz without chiral doping in a 3 μ m homeotropic cell. The polymer solid was annealed at 95 °C (nematic phase) for 12 h after slowly cooled from isotropic state.



Fig. S7 POM images of the N*-LC containing 9.01 mol% of Azo-*R*5 in an empty cell. The mixture was annealed at 95 °C for 12 h after slowly cooled from isotropic state.



Fig. S8 POM images of the PAz doped with 6.25 mol% of Azo-*R*5 (a), Azo-*S*5 (b); 4.76 mol% of Azo-*R*5 (c), Azo-*S*5 (d); 3.84 mol% of Azo-*R*5 (e), Azo-*S*5 (f) in a 3 μ m homeotropic cell. The solid mixture was annealed at 95 °C (nematic phase) for 12 h after slowly cooled from isotropic state.



Fig. S9 The X-ray profiles of the PAz doped with 4.76 mol% Azo-*R5* (a) and Azo-*S5* (b). The mixture solid was annealed at 95 °C (nematic phase) for 12 h after slowly cooled from isotropic state.



Fig. S10 CD spectra of polymer films (PAz) doped with 9.01 mol% Azo-*R5* (a), Azo-*S5* (b) and changes in the maximum CD (c) and g_{CD} values (d) during the heating process.



Fig. S11 CD and UV-vis spectra of polymer films (PAz) doped with different content of Azo-*R*5 (a) and Azo-*S*5 (b).



Fig. S12 (a) ¹H NMR spectra of redisual chiral dopant in the soaking solution, which was changed after each measurement. (b) ¹H NMR spectra and (c) HPLC spectra of the chiral polymer film measured before and after removal of chiral dopant. (d) CD and UV-vis spectra of the N*-LC measured before and after removing the dopant.

Probing the supramolecular helical direction in N*-LC by LD spectroscopy. According to the reported results by Meijer *et al.*⁴, thin polymer films of PAz doped with 4.76 mol% chiral molecules were prepared by spin-coating the solution onto a clean planar rubbed polyimide glass slides (12 mg/mL in THF, following a speed of 0.5 rpm for 6 seconds and a speed of 1.9 rpm for 20 seconds. thickness: 100-200 nm). Then the films were annealed at 95 °C to obtain the USH (uniform standing helix) structure. What can be firmly believed is that the USH is imcomplete and less than quarter of the full helix due to the thickness is much shorter than the helical pitch (3.9 μ m). Three orientation were chosen: horizontal, roate 45° to the right and roate 45° to the left. First, the handedness of the N*-LC arrangement of the Paz doped with Azo-*R*5 was determined by analyzing linear dichroism (LD) spectra. As shown in

Fig. S13a, dOD of the horizontal is positive at the absorption maximum, means that the polymer side chains are mostly aligned in the horizontal direction (LD (dOD) = OD// - OD \perp = log ($I \perp / I_{//}$), $I \perp$ stands for the energy of vertical polarized transmitted light and $I_{//}$ stands for the energy of horizontally polarized transmitted light). Upon rotating the thin film over 45° in the clockwise direction, dOD value is negative. This indicates that the helical stacking direction is the same as the rotating direction, which corresponds to a right-handed cholesteric arrangement. The result is similar to the thin film doped with Azo-S1 and the helical direction of the films doped with Azo-S5 and Azo-R1 judged by LD spectra is left-handed.

Fig. S13 Linear dichroism (LD) profiles for the N*-LC doped with different chiral dopants measured at different direction.

Fig. S15 CD and UV-vis spectra of polymer films (PAz-*r*-AzOH) doped with 9.01 mol% Azo-*R*5 (a), Azo-*S*5 (b) and changes in the g_{CD} values (c) during the heating process. (d) POM images of the N*-LC containing PAz-*r*-AzOH and 9.01 mol% of Azo-*R*5 (annealled in nematic for 12 h) in an empty cell.

Fig. S16 Changes in O 1s (a) and full (b) XPS spectra of polymer film (PAz-*r*-AzOH) recorded before and after cross-linking.

Fig. S17 Changes in the CD spectra of the cross-linked and uncross-linked chiral films after heating beyond the clearing temperature and cooling down to roomtemperature.

Fig. S18 Changes in the CD and UV-vis spectra of the chiral polymer films (PAz-*r*-AzOH) during 365 nm light irradiation and heating-cooling process. The films are measured before removing the dopants and before cross-linking. (a), (b) induced by Azo-*R*5; (c), (d) induced by Azo-*S*5.

Fig. S19 Changes in the CD and UV-vis spectra of the chiral polymer films (PAz-*r*-AzOH) during 365 nm light irradiation and heating-cooling process. The films are measured after removing the dopants and before cross-linking. (a), (b) induced by Azo-*R*5; (c), (d) induced by Azo-*S*5.

Fig. S20 Changes in the CD and UV-vis spectra of the chiral polymer films (PAz-*r*-AzOH) during 365 nm light irradiation and heating-cooling process. The films are measured after removing the dopants and after cross-linking. (a), (b) induced by Azo-*R*5; (c), (d) induced by Azo-*S*5.

Fig. S21 Changes in the CD and UV-vis spectra of the chiral polymer films (PAz-*r*-AzOH) in the switch of 365 nm light irradiation and heating-cooling process. The films are measured after removing the dopants and after cross-linking. (a) induced by Azo-*R*5; (b) induced by Azo-*S*5.

3. References

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