ADVANCED MATERIALS

Supporting Information

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Surfaces Decorated with Enantiomorphically Pure Polymer Nanohelices via Hierarchical Chirality Transfer across Multiple Length Scales

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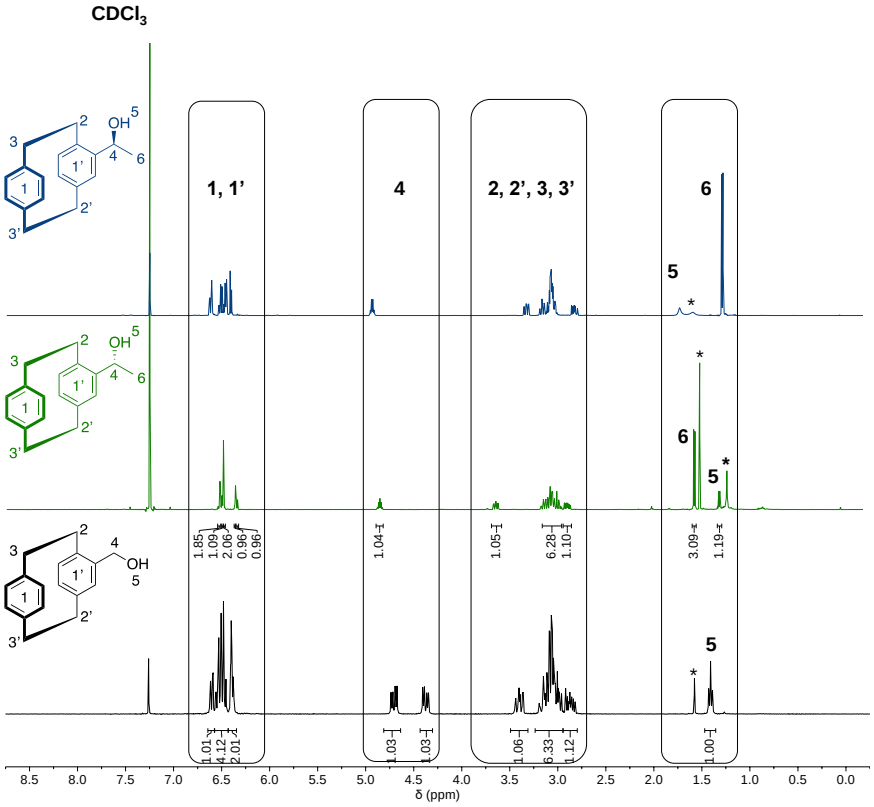


Figure S1. **^{1}H NMR spectra of 1S-R/1A**. ^{1}H NMR spectrum of **1S** (top), **1R** (middle), and **1A** (bottom).

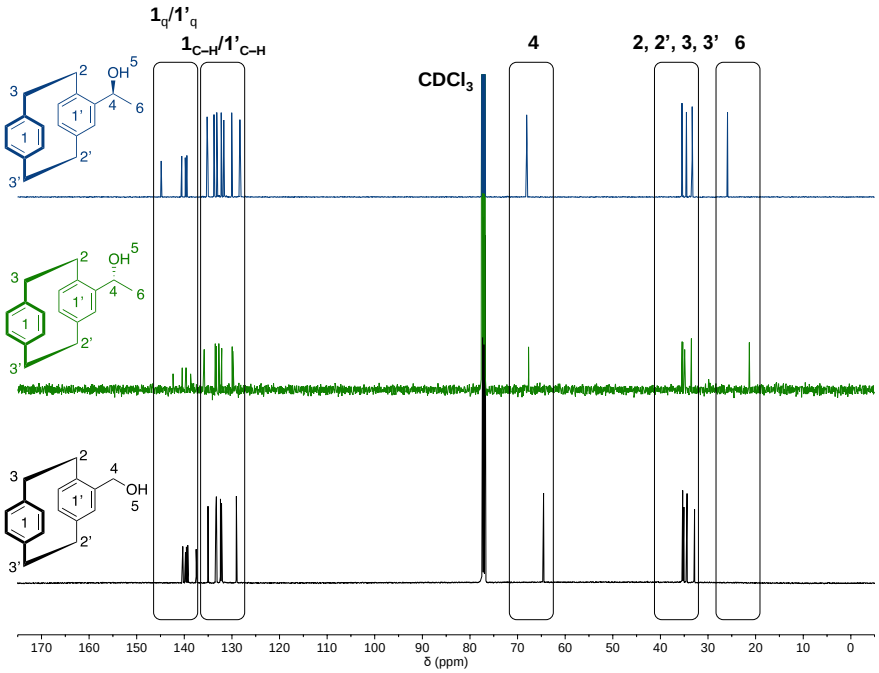


Figure S2. **^{13}C NMR spectra of 1S-1R/1A**. ^{13}C NMR spectrum of **1S** (top), **1R** (middle), and **1A** (bottom).

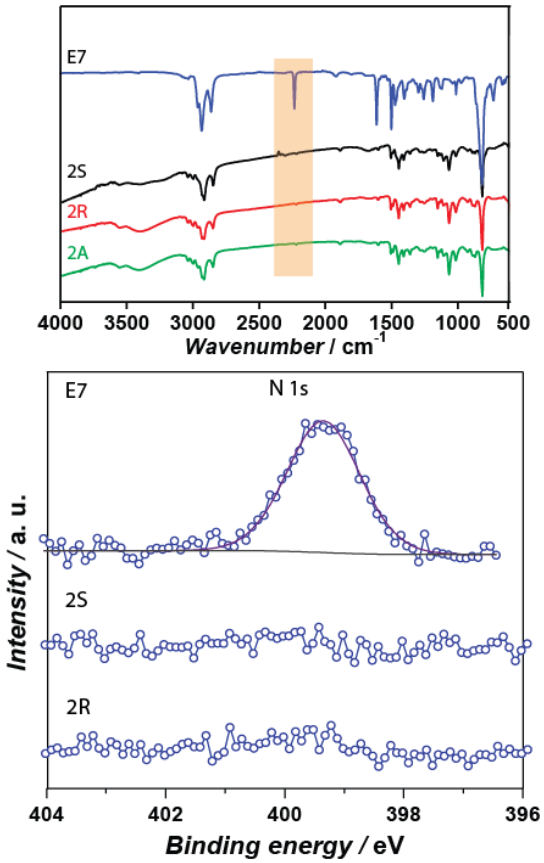


Figure S3. **IRRAS and XPS spectra showing the complete removal of LCs after the formation of nanohelices. (A)** IRRAS spectra of (blue) E7, (black) polymer **2S**, (red) polymer **2R**, and (green) polymer **2A** nanohelices templated in E7. **(B)** XPS high-resolution N1s spectrum of pure E7 (top), polymer **2S** (middle), and polymer **2R** (bottom) nanohelices. LC was removed prior to all measurements.

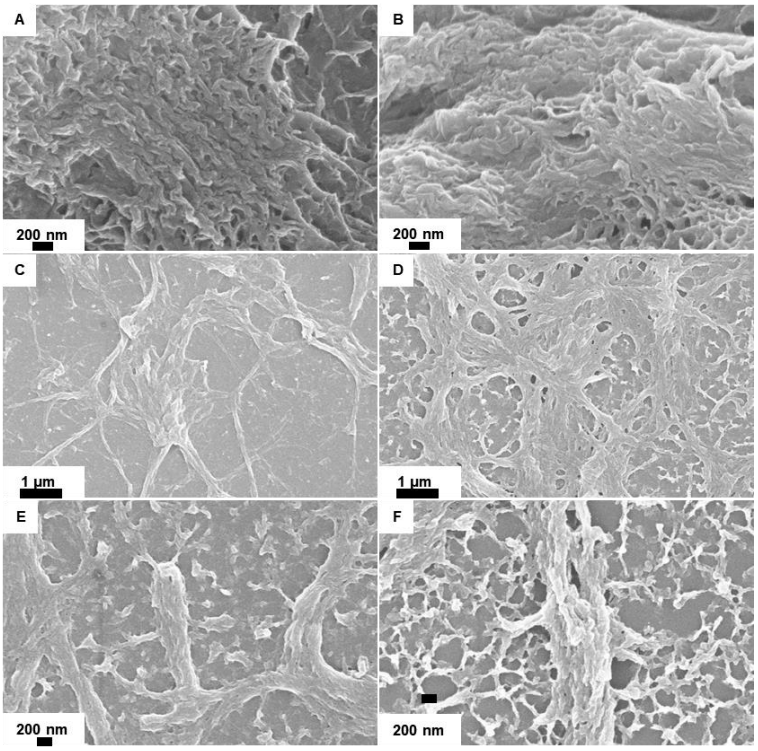


Figure S4. CVD polymerisation of chiral 2.2[Paracyclophanes] consisting of bulky side groups. (A,B) CVD polymerisation of S_pS and S_pR PCP(CHOMeMe)), (C,D) (PCP(CHOHiPr)), and (E,F) (PCP(CHOHPh), respectively into a E7 as a nematic LC template.

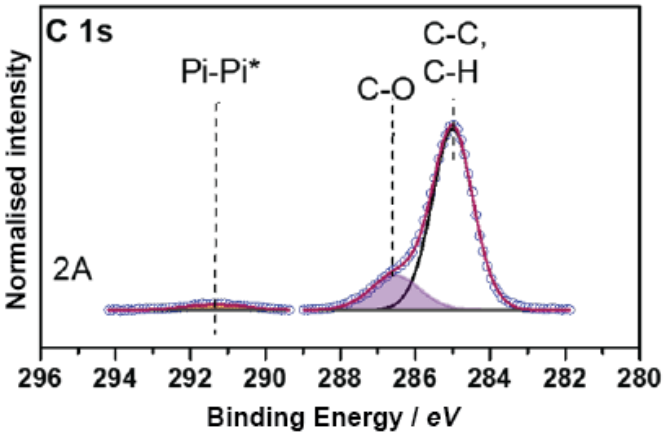


Figure S5. High-resolution C1s XPS spectra of **2A** nanofibers confirming identical chemical composition to that of **2S** and **2R** nanohelices.

(C-O)/ [(C-C,C-H) + (π-π*)]	Fiber	Film
2S	0.14	0.10
2R	0.14	0.10

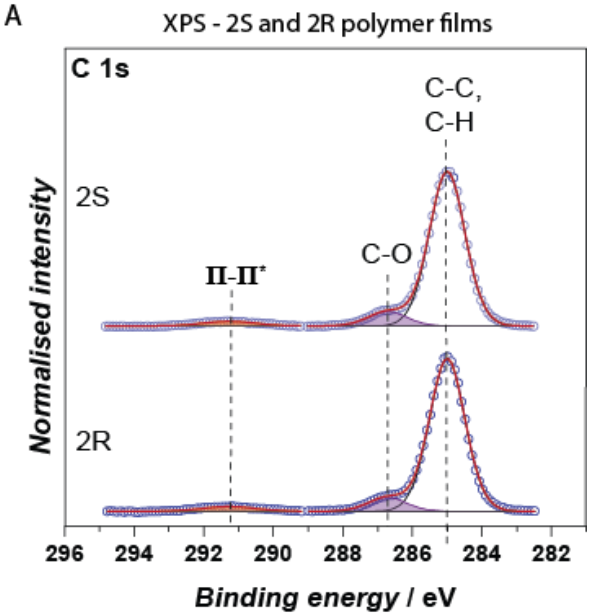
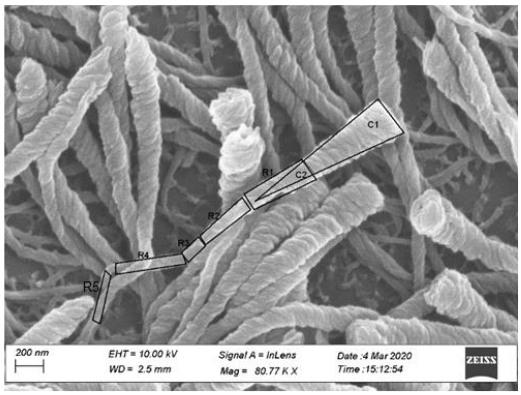


Figure S6. **XPS spectra of chiral polymer films and their comparison to 2S,2R,2A nanohelices showing the structural similarity. (Top)** Comparison of the atomic % ratio of [C-O/(C-C,C-H+π-π*)] peaks in the XPS spectra. **(Bottom)** XPS high-resolution C1s spectra of **2S** (top) and **2R** (bottom) polymer films show C-C, C-H, C-O, and pi-pi* peaks.



diameter	radii	pitch	length	Contour length single NF (um)
0.2803	0.14015	0.0545	0.881828	9.735656
0.2803	0.14015	0.0545	0.881828	
0.2803	0.14015	0.0545	0.881828	
0.2314	0.1157	0.0545	0.728637	
0.2314	0.1157	0.0545	0.728637	
0.2058	0.1029	0.0545	0.648506	
0.2058	0.1029	0.0545	0.648506	
0.1689	0.08445	0.0545	0.533139	
0.1595	0.07975	0.0545	0.503787	
0.1595	0.07975	0.0545	0.503787	
0.1193	0.05965	0.0631	0.379879	
0.1193	0.05965	0.0631	0.379879	
0.1193	0.05965	0.0631	0.379879	
0.1123	0.05615	0.0631	0.358223	
0.1123	0.05615	0.0631	0.358223	
0.0773	0.03865	0.0631	0.25079	
0.0838	0.0419	0.0661	0.271307	
0.0685	0.03425	0.0661	0.225018	
0.0574	0.0287	0.0661	0.191975	

Single NF				NF bundle									
diameter (nm)	radius (nm)	radius (um)			diameter (nm)	Diameter (um)	radius (nm)	radius (um)	height (nm)	height (um)	Volume	NF vol	Contour length
50.4481	25.22405	0.02522405		C1	297.5844	0.2975844	148.7922	0.1487922	1091.2506	1.0912506	0.02528676	0.038508	19.27501251
				C2	105.2632	0.1052632	52.6316	0.0526316	424.3874	0.4243874	0.00123045		
				R1	157.6997	0.1576997	78.84985	0.07884985	465.3874	0.4653874	0.00908544		
				R2	82.2132	0.0822132	41.1066	0.0411066	393.1391	0.3931391	0.00208593		
				R3	84.5024	0.0845024	42.2512	0.0422512	166.2506	0.1662506	0.0009319		
				R4	70.5254	0.0705254	35.2627	0.0352627	483.9689	0.4839689	0.00188964		
				R5	41.0885	0.0410885	20.54425	0.02054425	346.3746	0.3463746	0.00045905		

Contour length (um) = NF volume/(3.14*(Single NF radius)^2)

Figure S7. Calculations describing the contour length of a single and a bundle of nanohelices from SEM images.

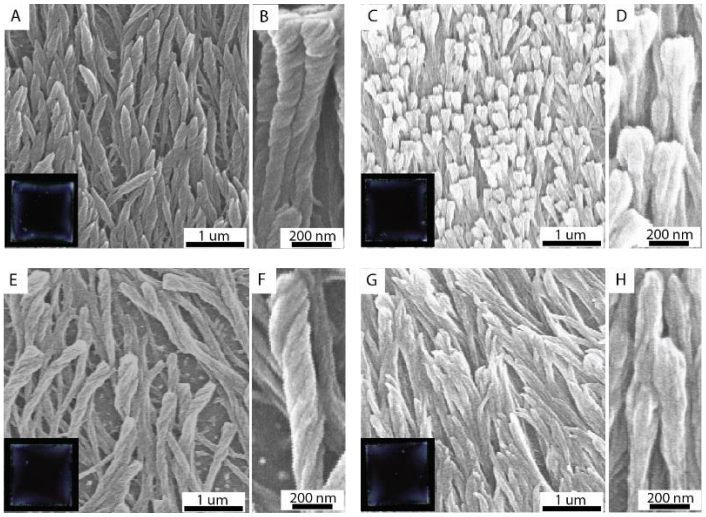


Figure S8. **The presence of a stereogenic center is a prerequisite for the formation of twisted nanohelices. (A-D):** SEM images of polymer nanohelices **2S** (A, B) and nanofibers **2A** (C, D) prepared by LC-templated CVD polymerisation using E7 doped with 2.28 wt% **1S**. **(E-H):** SEM images of polymer nanohelices **2S** (E, F) and nanofibers **2A** (G, H) prepared by LC-templated CVD polymerisation using E7 doped with 5.9 wt% S-DMPE. Shown in the insets are the polarized light micrographs of the templating LC phases before CVD polymerisation (homeotropic alignment).

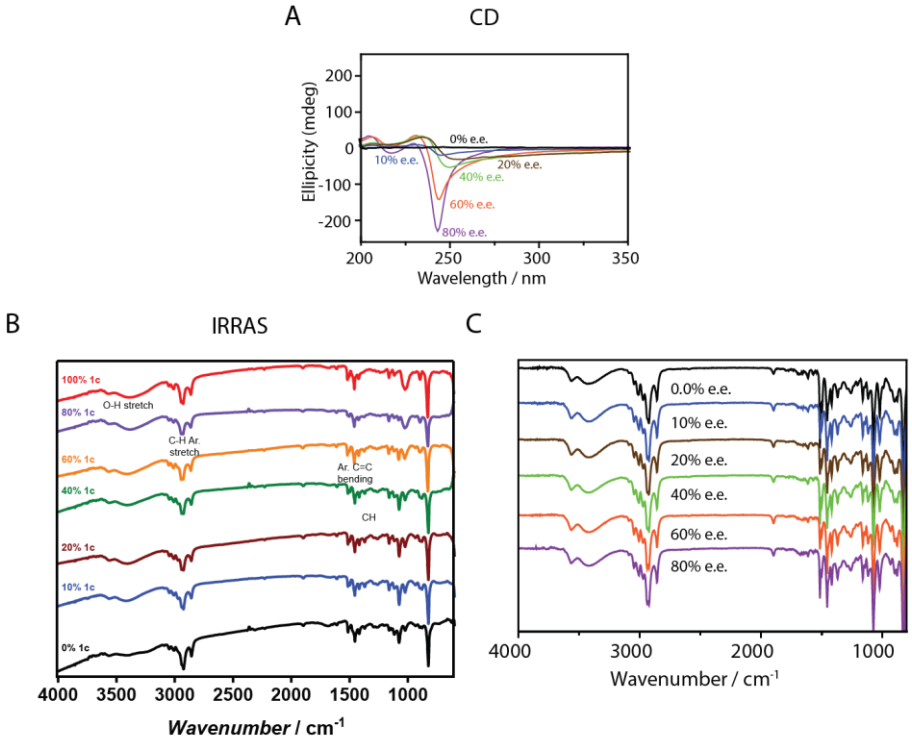


Figure S9. FTIR and CD spectra showing the effect of polymerising chiral precursors with varying enantiomeric purities. (A) CD spectra of polymer nanohelices prepared from different enantiomeric excesses of **1S**. (B,C) IRRAS spectra of polymers prepared with different monomer compositions **1S**+**1A** (A) and % E.E **1S** (B).

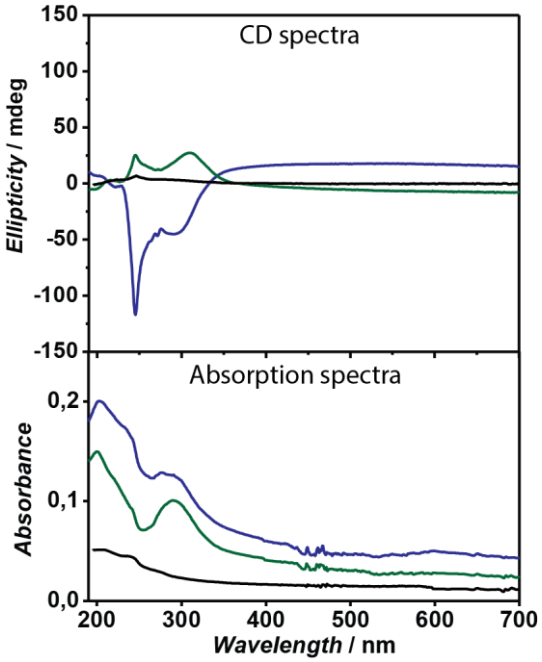


Figure S10. Solid-state CD and absorption spectra of 2S-2R/2A nanohelices. CD (top) and absorption (bottom) spectra of **2S** (blue), **2R** (green), and **2S+2R (1:1)** (black) polymer nanohelices.

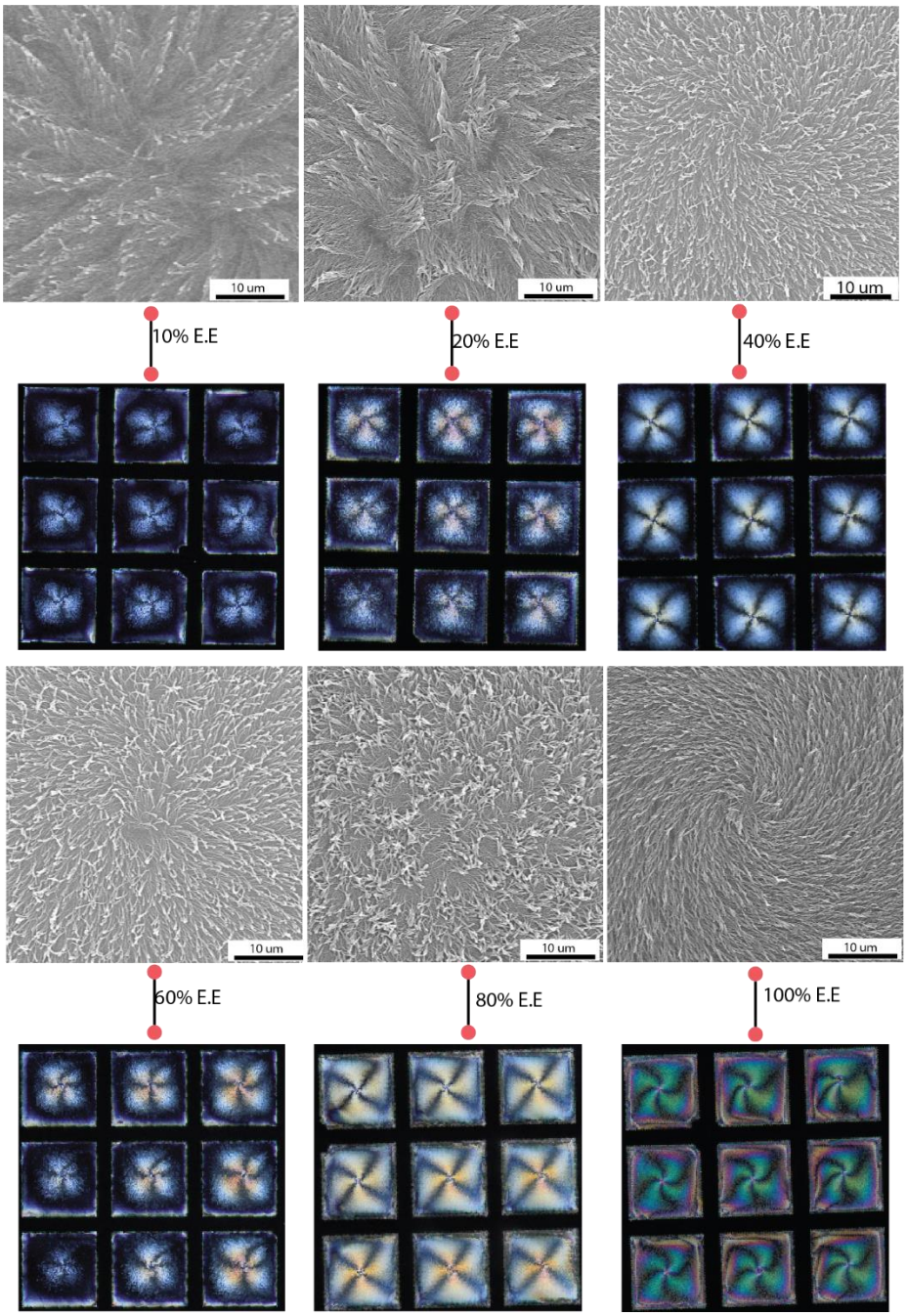


Figure S11. **Mesoscale structures of polymer nanohelices prepared from varying %E.E of 1S in E7.** SEM images of nanohelices prepared from 10-100% E.E (top) and the corresponding POM images (bottom).

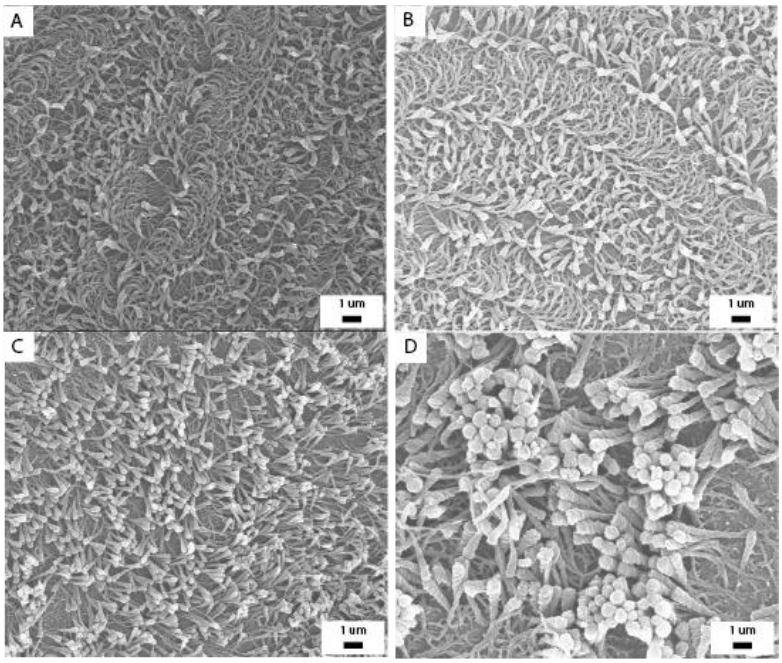


Figure S12. An overview of the synergistic effect (A and B) seen by polymerising **1S** and **1R** into E7+2.4% S-811 and E7+2.3% R811, respectively. Similarly, (C) and (D) show an overview of the antagonistic effect seen by polymerising **1S** and **1R** into E7+2.3% R-811 and E7+2.4% S811, respectively.

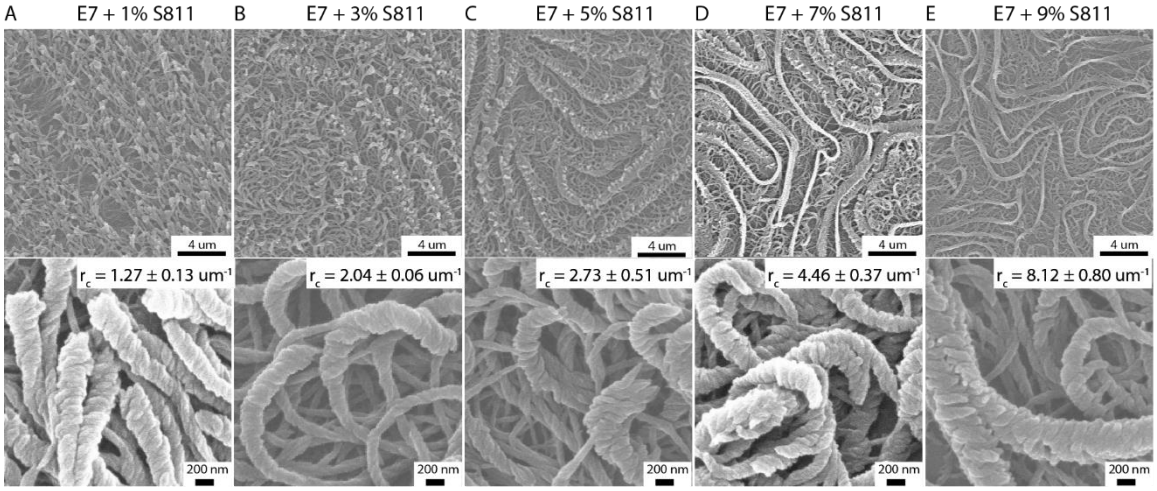


Figure S13. Effect of polymerising **1S** into E7 + x% S811. SEM images showing the mesoscale arrangement of twisted chiral nanohelices bundles (top) and magnified images of individual twisted nanohelices bundles representing the twist direction (CCW). The radius of curvature of the nanohelices bundles is represented as r_c values.

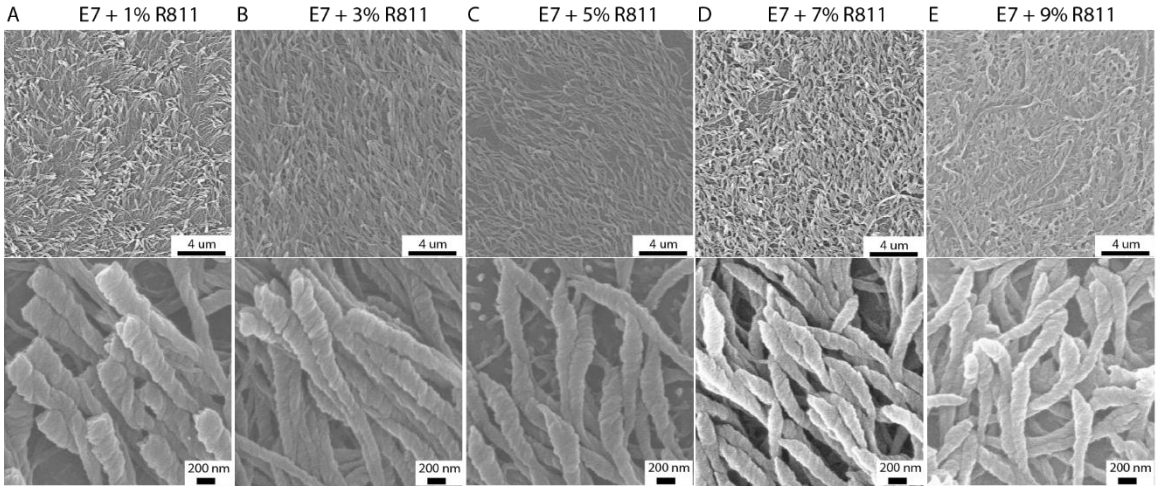


Figure S14. Effect of polymerising **1S** into E7 + x% R811. SEM images showing the mesoscale arrangement of twisted chiral nanohelical bundles (top) and magnified images of individual twisted nanohelical bundles representing the clockwise twist direction.

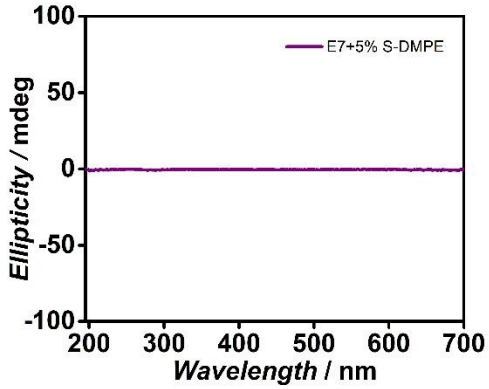


Figure S15. CD spectrum of E7+5% S-DMPE

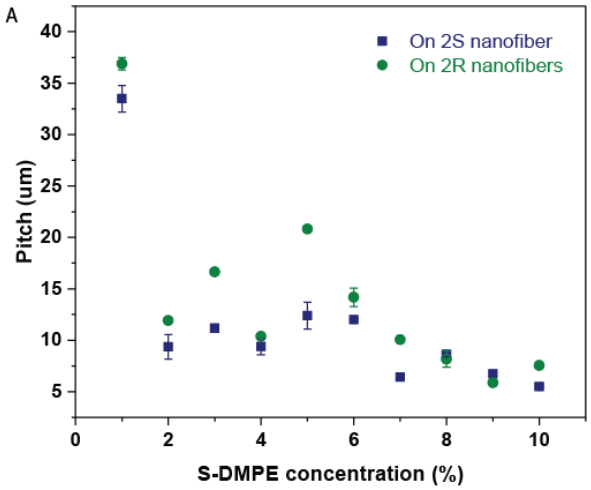


Figure S16. **Pitch values of LC mixtures on chiral nanohelical substrates. (A):** Pitch values of E7 + 1-10% S-DMPE on **2S** (blue) and **2R** (green) array of nanohelices.

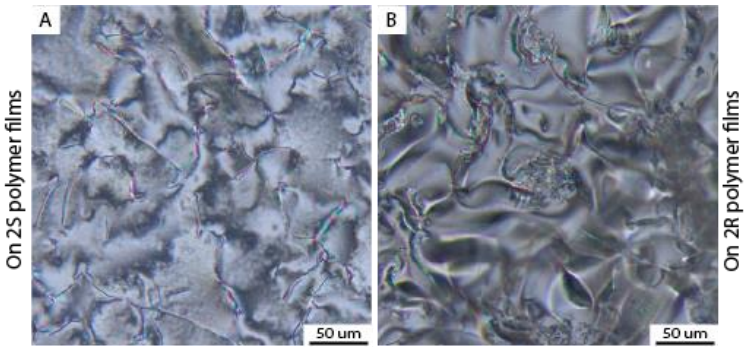


Figure S17. **Behavior of E7 + 5% S-DMPE on chiral polymer films**. LC textures of E7 + 5% S-DMPE on **2S** (A) and **2R** (B) polymer films.