

Supporting Information

Facile Emission Color Tuning and Circularly Polarized Light Generation of Single Luminogen in Engineering Robust Forms

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Experimental Section

Binary polymeric materials for emission color tuning. Polystyrene (PS, $M_w = 1.0 \times 10^5$ g mol⁻¹, Sigma Aldrich) and polybutadiene (PB, $M_w = 2.0 \times 10^5$ g mol⁻¹, Sigma Aldrich) were dissolved in toluene to form a 5 mg mL⁻¹ solution, respectively. PDHA and TDHA were synthesized according to the literature methods.¹ The emission color was controlled by tuning the polymer rigidity. The procedures using TDHA for color tuning were given below as an example. TDHA was first dissolved in toluene to generate a 10 mg mL⁻¹ stock solution. Then 10 μ L of TDHA solution was combined with 200 μ L of polymer blend solution under continuous stirring. The polymer blend solutions with different PS mass fractions were prepared by mixing PS and PB stock solution accordingly. Afterward, the resulting solutions with different polymer compositions were spin-coated on quartz glass slides followed by heating to exclude the solvent in the films for next PL and microscopic study. Same procedures were employed by using PDHA to obtain color tunable materials.

Fabrication of white-emissive P-PS. A mixture of PDHA and PS (1:10, w/w) was dissolved in THF to form a stock solution. The solution of P-PS was drop-casted on a PTFE mold followed by solvent evaporation. The resulting film was cut into desired size (diameter = 11 mm) to integrate with UV LED flashlight. The P-PS concentrated solution (25 mg mL⁻¹) was also used to coat film onto the outer surface of plastic optical fiber to form an emissive layer.

Fabrication of white-emissive T-SB fibers. The T-SB fibers were fabricated using continuous wet-spinning method. First, a mixture of TDHA and poly(styrene-co-butadiene) (SB, styrene 45 wt%, Sigma Aldrich) in a weight ratio of 1:10 was dissolved in THF solution to form a homogenous solution (25 mg mL^{-1}). Then, the above solution was used as spinning dope and transferred to a syringe with a needle (needle gauge: 25 mm; the inner diameter: 0.8 mm), followed by injecting into ethanol as coagulation bath at a flow rate of 30 mL h^{-1} . Last, continuous fibers were collected onto a polytetrafluoroethylene (PTFE) guide roll (diameter = 8 mm). The continuous wet-spinning was carried out on the home-made apparatus illustrated in [Figure S9a](#). The collected fibers ([Figure S9b](#)) were further wound onto a glass vials for tensile test and UV LED integration.

Fabrication of P-PLLA with white CPL property. A mixture of poly(L-lactide) (PLLA, $M_w = 8.9 \times 10^4 \text{ g mol}^{-1}$) and PDHA (1:10, w/w) was dissolved in chloroform to form a solution (10 mg mL^{-1}). Crystallization of polymer occurred via slow solvent evaporation at ambient temperature. Then, the thin, crystalline P-PLLA film with a desired thickness was peeled off from the substrate of container.

Measurements. Microscopic images were taken on a Nikon Eclipse 80i microscope. Fluorescence spectra were performed on a HORIBA Fluorolog-3 research spectrofluorometer. Lifetime measurements were carried out on a PTI TimeMaster fluorometer at 430 and 530 nm under 385 nm excitation. Differential scanning calorimetry (DSC) measurements was carried out under nitrogen using a Mettler-Toledo HP DSC1 system operating at a heating and cooling rate of $10 \text{ }^{\circ}\text{C min}^{-1}$ in the range of 0-150 $^{\circ}\text{C}$ and -70-0 $^{\circ}\text{C}$, respectively. Atomic force microscopy (AFM, Ntegra Prima, NT-MDT Spectrum Instruments) was performed under tapping mode using silicon cantilevers at a scan rate of 1 Hz. UV-vis and CD spectra were collected on an Applied Photophysics Chirascan Spectrometer. CPL spectra were obtained on JASCO CPL-

300, the measurement conditions of CPL measurements are listed in Table S1. The thickness of the composite film for CPL tests is controlled to be ~50 μm . The stretchable films and fibers were cut into small pieces for tensile tests on an INSTRON 5564 at a speed of 20 mm min^{-1} . X-ray Diffraction measurement of the crystalline P-PLLA film was carried out on a Rigaku D/max-2550.

Table S1. The measurement conditions of CPL measurements on CPL-300 instrument.

Measurement Conditions (CPL)	
Excitation Wavelength	340 nm
Excitation Slit Width	3 mm
Data Pitch	0.1 nm
Emission slit width	3 mm
Scan Speed	50 nm/min
D.I.T.	8 sec

Table S2. Photophysical properties of TDHA and PDHA in the aggregated states.¹

sample	λ_{em} (nm)	Φ_{F} (%)	τ (ns)
TDHA-c	425	27.7	0.86
THDA-am	520	3.3	0.43
PDHA-c	446	15.1	0.85

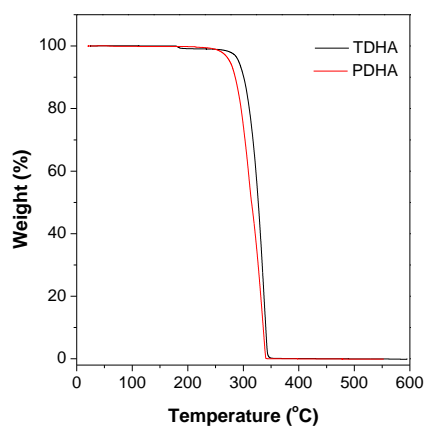


Figure S1. TGA thermograms of TDHA and PDHA recorded under nitrogen at a heating rate of 10 $^{\circ}\text{C min}^{-1}$.

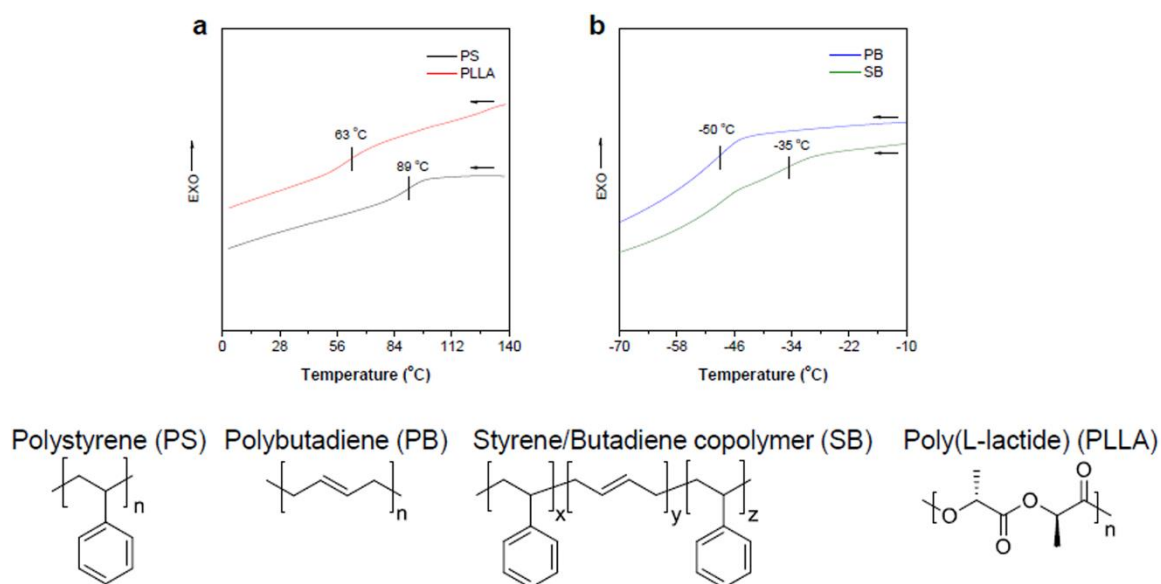


Figure S2. DSC thermograms of the polymers recorded under nitrogen at the second cooling scan at a rate of $10\text{ }^{\circ}\text{C min}^{-1}$.

The glass transition temperature (T_g) manifests the flexibility of the polymer chain. Polymers with high rigidity often show high T_g . The commercially available polystyrene (PS) and polybutadiene (PB) were used as representative rigid and soft matrices in this study and their T_g measured by DSC analysis was $89\text{ }^{\circ}\text{C}$ and $-50\text{ }^{\circ}\text{C}$, respectively.

As shown in [Figure 3c](#) and [3d](#) in the main text, the CIE coordinates (0.30, 0.36) emission of PDHA embedded in pure PS network is quite close to those of pure white color. On the other hand, poly (L-lactide) ($T_g = 63\text{ }^{\circ}\text{C}$) shows a rigidity comparable with that of PS ($T_g = 89\text{ }^{\circ}\text{C}$). When embedded PDHA in PLLA, the rigid amorphous fraction of PLLA serves as the environment similar to that of PS to generate white emission.

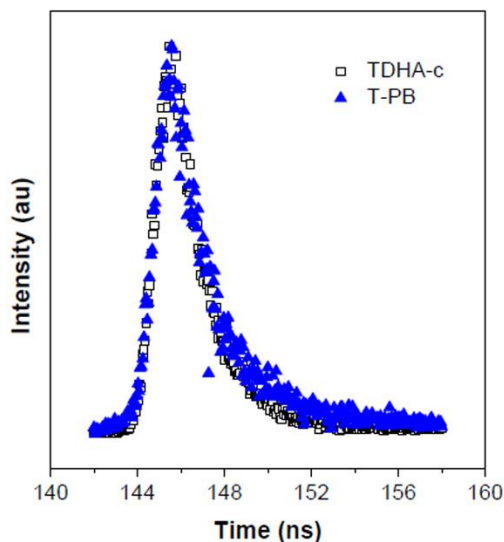


Figure S3. PL decay curves of TDHA-c and T-PB film at 430 nm. Excitation wavelength: 385 nm.

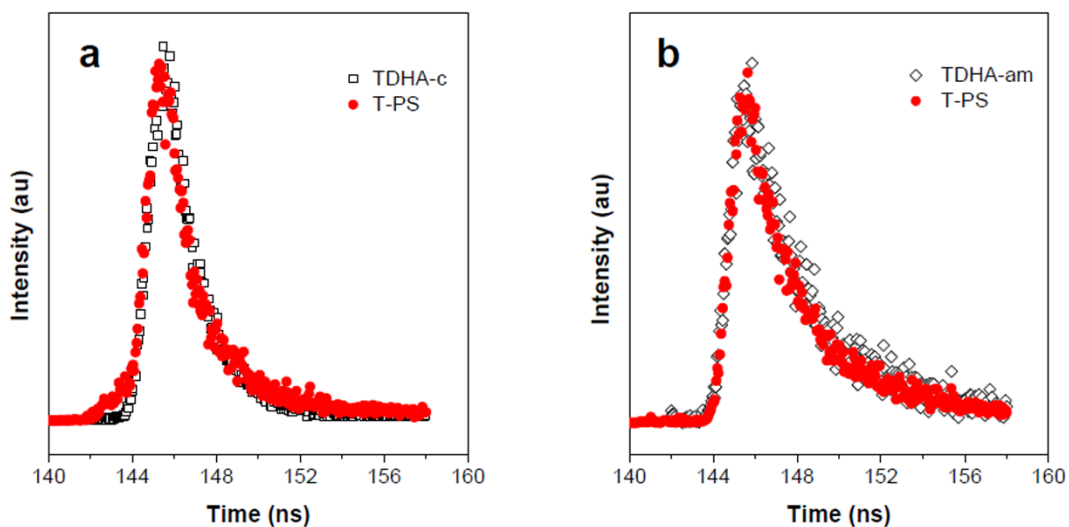


Figure S4. PL decay curves of (a) TDHA-c and T-PS at 430 nm, and (b) TDHA-am and T-PS at 530 nm. Excitation wavelength: 385 nm.

In Figure S3 and S4, the shorter-lived excited states dominate the measurements conducted at 430 nm, while the longer-lived excited ones contribute predominantly to the decay curves recorded at 530 nm. Thus, the emission of T-PB comes from the TDHA-c species, while the emission of T-PS results from both TDHA-c and TDHA-am species.

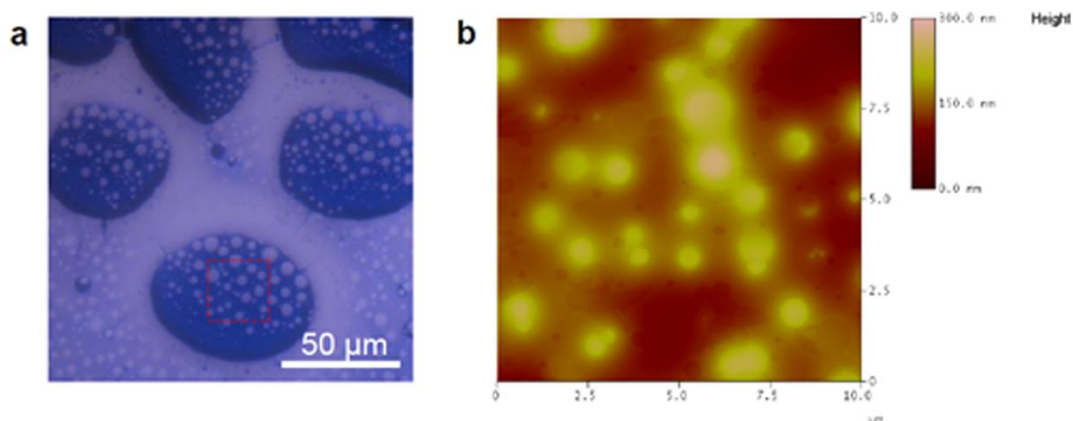


Figure S5. (a) Fluorescence image showing the phase separation of TDHA-doped PS/PB film with $\phi(\text{PS}) = 60\%$. (b) Magnified image of the marked area in Figure (a) using AFM.

When $\phi(\text{PS})$ increased to 60%, a “salami” morphology was obtained as shown in [Figure S5a](#). The magnified area in [Figure S5a](#) was scanned by AFM ([Figure S5b](#)), which further demonstrated that the redder emissive domains were constituted by the PS matrix.

Table S3. Corresponding CIE 1931 coordinates of AIEgen-assembled PB/PS samples.

PS/PB ratio	TDHA		PDHA	
	x	y	x	y
0:10	0.18	0.17	0.18	0.16
1:9	0.18	0.17	0.19	0.18
2:8	0.24	0.28	0.21	0.20
3:7	0.27	0.32	0.22	0.23
4:6	0.26	0.31	0.24	0.27
5:5	0.26	0.31	0.24	0.27
6:4	0.28	0.34	0.28	0.34
7:3	0.27	0.33	0.30	0.36
8:2	0.27	0.33	0.30	0.37
9:1	0.28	0.35	0.30	0.36
10:0	0.27	0.32	0.30	0.36

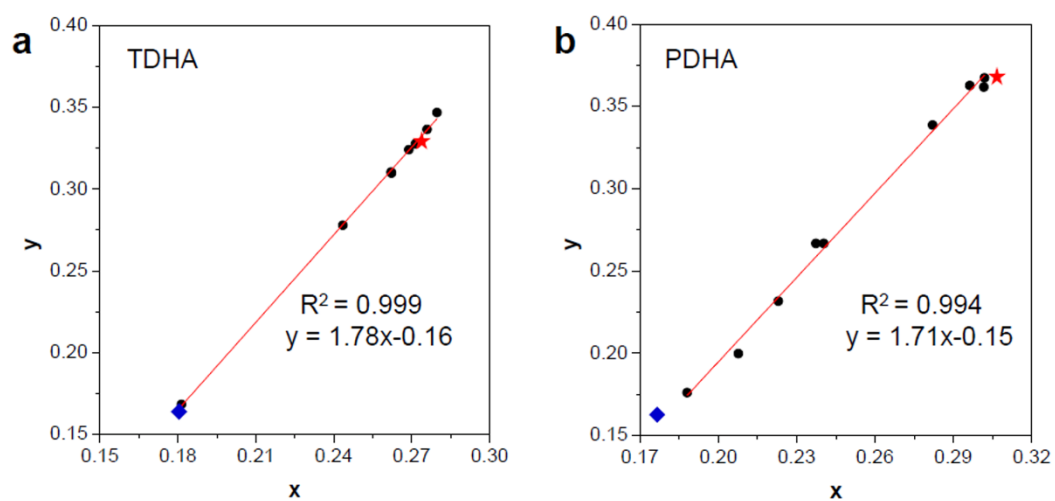


Figure S6. Corresponding CIE 1931 coordinates of (a) TDHA and (b) PDHA-doped PB/PS samples.

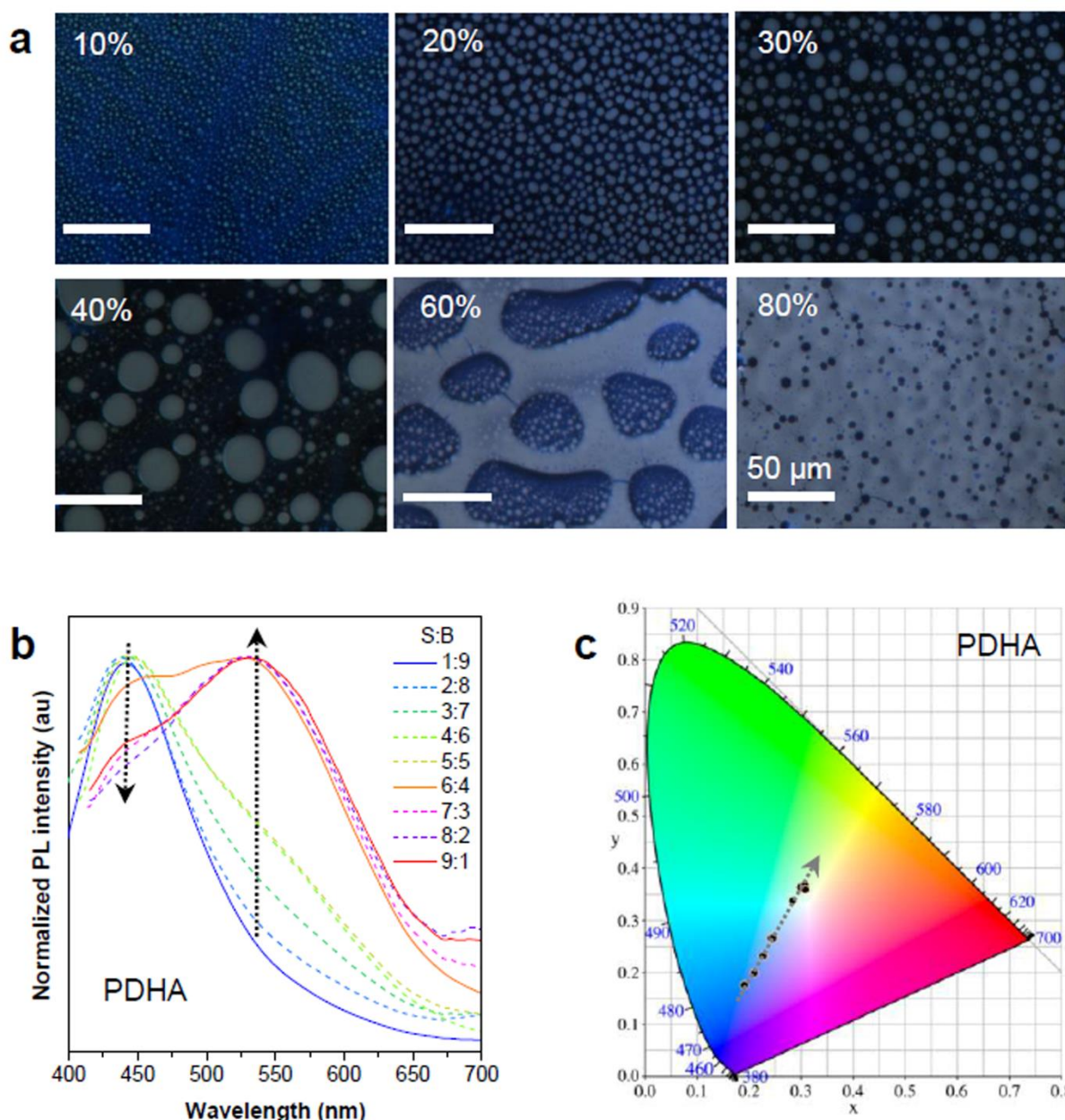


Figure S7. (a) Morphological revolution of microphase separation of PDHA-doped PB/PS film by increasing the mass fractions of PS ($\phi(\text{PS})$). The photos were taken on fluorescent microscope with UV light excitation. (b) Normalized PL spectra of PDHA-doped PB/PS films with different $\phi(\text{PS})$. Excitation wavelength: 370 nm. (c) Corresponding CIE 1931 coordinates in CIE-1931 chromaticity diagram of PDHA-doped PB/PS samples.

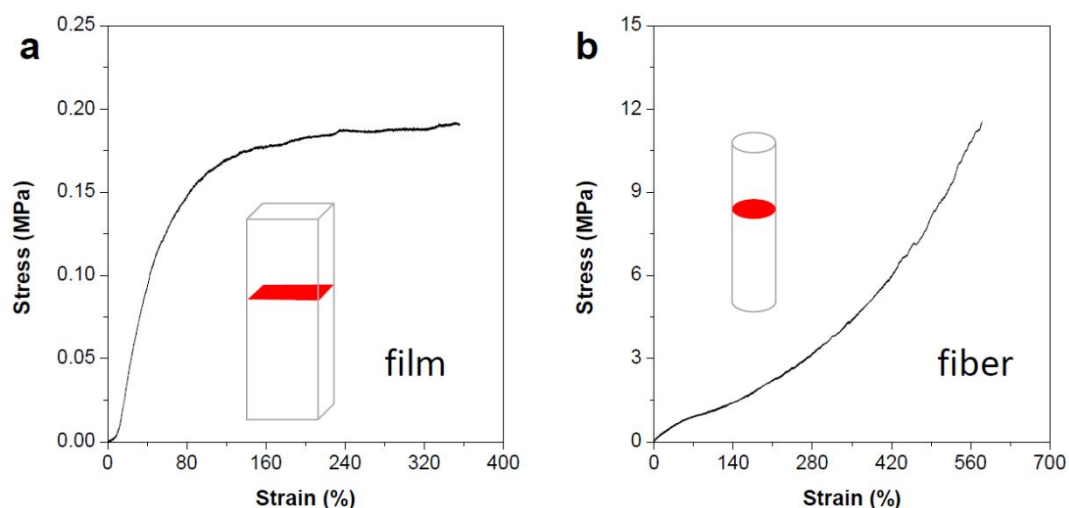


Figure S8. Representative stress-strain curves of T-SB-based (a) film and (b) fiber.

The T-SB-based film and fiber samples were cut into small strips with length of 10 mm. The cross-sectional areas of the two samples are 1.4 and 0.050 mm², respectively. Both samples show good ductility with large strain of ~350% and 580%. The T-SB-based fibrous material shows obvious improvement in elongation at break and breaking strength compared with that of film-based sample, owing to the alignment of the polymer chain during the fiber spinning process.

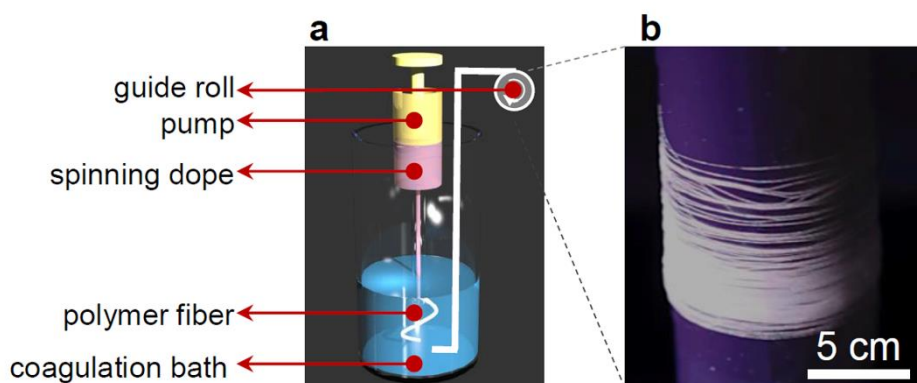


Figure S9. (a) Schematic illustration of the wet-spinning set-up and (b) the fluorescence image of the as-spun T-SB fibers.

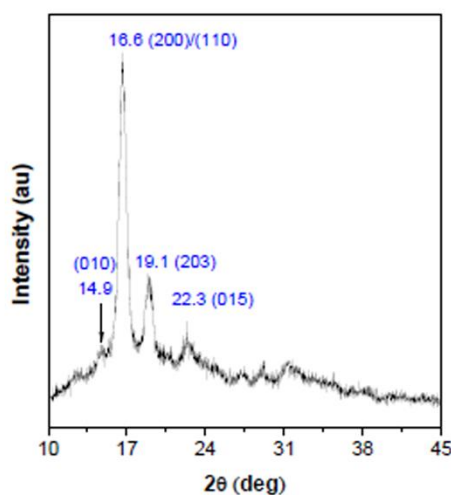


Figure S10. XRD pattern of the crystalline P-PLLA composite film.

The diffraction peaks shown in Figure S10 are characteristic of the α -crystalline phase of PLLA. The peaks at $2\theta = 14.9^\circ$, 16.6° , 19.1° and 22.3° correspond to the lattice planes (010), (200)/(110), (203) and (015), respectively.²

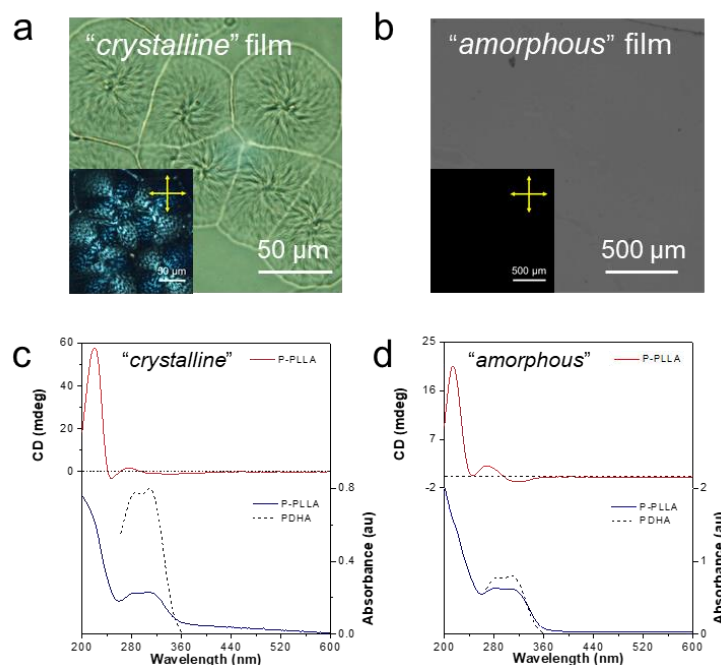


Figure S11. (a, b) Microscopic images of (a) the “crystalline” and (b) “amorphous” P-PLLA films. (c, d) UV spectra and corresponding CD spectra of the (c) “crystalline” and (d) “amorphous” P-PLLA films. The thickness of the P-PLLA for CD measurements is controlled to be less than 5 μm .

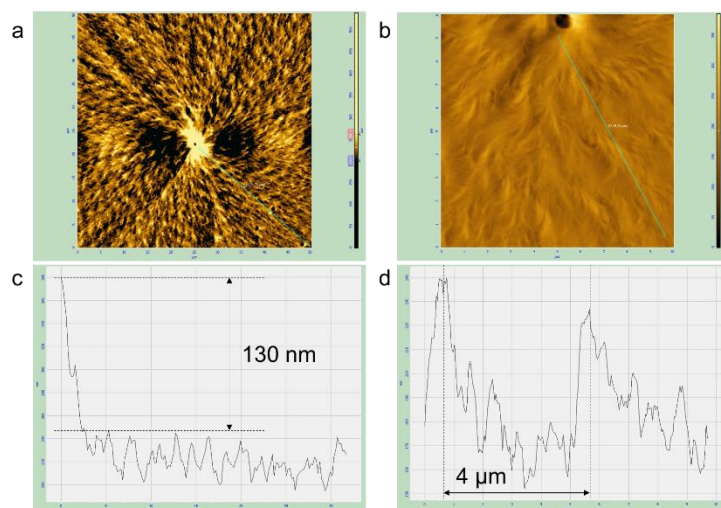


Figure S12. (a) AFM topography. (b) The magnified image in the center region revealing the periodic twisting of crystalline lamellae along the radial direction of the spherulites.³ (c, d) Cross sectional profiles along the line added in (a) and (b), respectively.

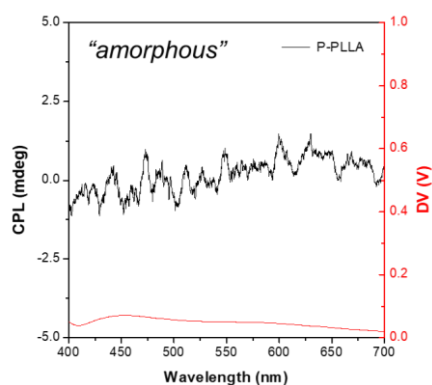


Figure S13: The CPL spectra “amorphous” P-PLLA film showing silent CPL response. Excitation wavelength: 340 nm.

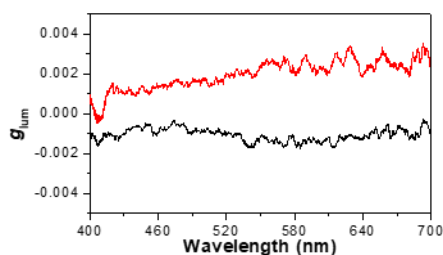


Figure S14. CPL dissymmetry factor g_{lum} as a function of the wavelength. The spectra were recorded on the same film but excited from two different sides.

References

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- (2) H. Xu, G. J. Zhong, Q. Fu, J. Lei, W. Jiang, B. S. Hsiao and Z. M. Li, *ACS Appl. Mater. Interface*, 2012, **4**, 6774.
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