

Supplementary Information

Extrusion-induced topological evolution mediated polymer-based flexible full-color circularly polarized luminescent materials towards 3D printing

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1. Supplementary Methods

Design and synthesis of the monomer and polymers

Synthesis of F-Octene monomer

First, 2,7-dibromofluorene (2.31 g, 7.13 mmol) was dissolved in 50 mL of dimethyl sulfoxide (DMSO), and the resulting solution was transferred into a 250 mL three-necked flask followed by vigorous stirring for over 30 min to achieve complete dissolution. Potassium hydroxide (KOH) powder (2.4 g, 42.77 mmol) was then added, and the mixture was stirred for an additional 10 min prior to the slow dropwise addition of 8-bromo-1-octene (3.00 g, 15.70 mmol). After the reaction proceeded for 12 h, the reaction mixture was poured into 20 mL of ice water, and the aqueous layer was extracted three times with 50 mL of ethyl acetate (EA). All organic extracts were combined, washed with saturated brine, and dried over anhydrous sodium sulfate. The crude product was further purified via column chromatography using n-hexane as the eluent to afford F-Octene as a transparent oily liquid (2.51 g) with a yield of 47%.

Synthesis of PFO-BT (P1)

Typically, the as-synthesized monomer F-Octene (200 mg, 0.367 mmol), 2,7-dibromo-9,9-di-n-octylfluorene (1.82 g, 2.77 mmol), 4,7-dibromo-2,1,3-benzothiadiazole (43.2 mg, 0.147 mmol), and 2,2'-bipyridine (1.15 g, 7.224 mmol) were sequentially added into a Schlenk tube. Subsequently, bis(1,5-cyclooctadiene)nickel(0) catalyst (1.96 g, 7.34 mmol) and tetrahydrofuran (15 mL) were transferred into the Schlenk tube inside a vacuum glove box, and the reaction mixture was heated at 60 °C for 36 h. Upon completion of the polymerization, the crude reaction mixture was poured into 500 mL of methanol/hydrochloric acid mixed solvent (20:1, v/v) for precipitation, followed by suction filtration to collect the crude polymer solid. The crude product was subjected to Soxhlet extraction with acetone as the eluent for three days. After extraction, the solid was dried under vacuum at 30 °C for 12 h to afford the achiral polyfluorene derivative P1 as a yellow solid (1.31 g) with a yield of 65%.

Synthesis of PFO (P2)

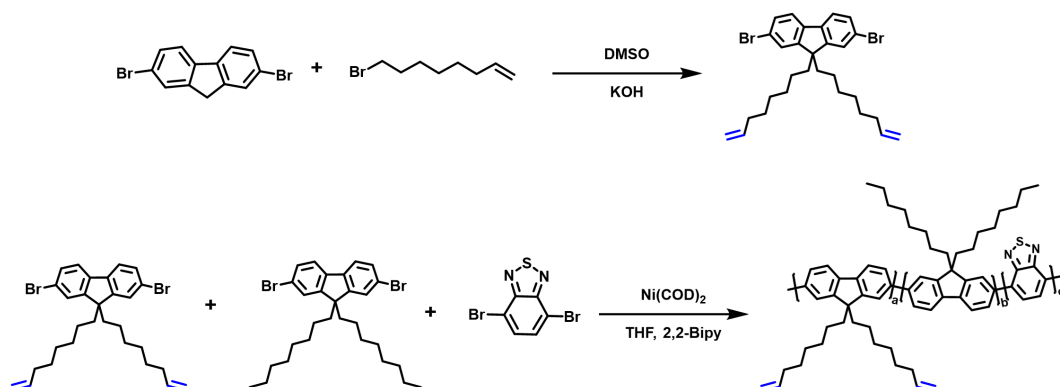
Similarly, the pre-synthesized monomer F-Octene (200 mg, 0.367 mmol), 2,7-dibromo-9,9-di-n-octylfluorene (1.82 g, 2.77 mmol), and 2,2'-bipyridine (1.15 g, 7.22 mmol) were sequentially

charged into a Schlenk tube. Afterwards, bis(1,5-cyclooctadiene)nickel(0) catalyst (1.96 g, 7.34 mmol) and tetrahydrofuran (15 mL) were transferred into the Schlenk tube within a vacuum glove box, and the mixture was heated to 60 °C and allowed to polymerize for 36 h. After the polymerization finished, the crude reaction mixture was poured into 500 mL of methanol/hydrochloric acid mixed solution (20:1, v/v) to precipitate the polymer, and the crude solid was collected via suction filtration. The crude product was purified by Soxhlet extraction using acetone as the extractant for three days. The obtained solid was subsequently dried in a vacuum oven at 30 °C for 12 h, delivering the achiral polyfluorene derivative P2 as a solid (1.80 g) with a yield of 72%.

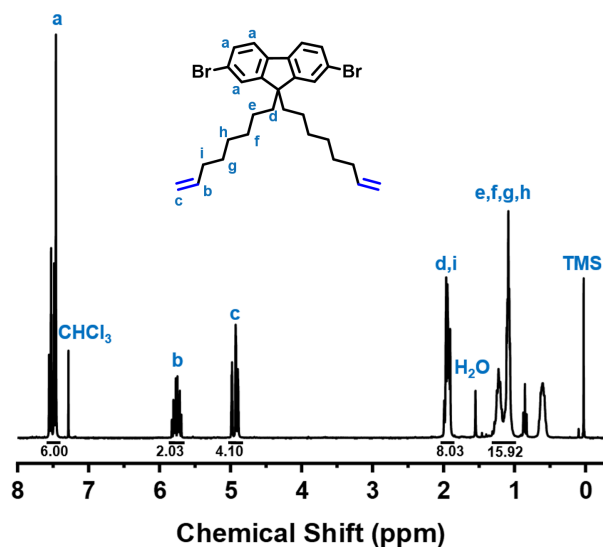
Synthesis of PFO-DTBT (P3)

Similarly, the pre-synthesized monomer F-Octene (200 mg, 0.367 mmol), 2,7-dibromo-9,9-di-*n*-octylfluorene (1.82 g, 2.77 mmol), 4,7-bis(5-bromo-2-thienyl)-2,1,3-benzothiadiazole (43.2 mg, 0.147 mmol), and 2,2'-bipyridine (1.15 g, 7.22 mmol) were sequentially loaded into a Schlenk tube. Afterwards, bis(1,5-cyclooctadiene)nickel(0) catalyst (1.96 g, 7.34 mmol) and tetrahydrofuran (15 mL) were transferred into the Schlenk tube inside a vacuum glove box, and the reaction mixture was heated at 60 °C for 36 h to complete polymerization. Upon termination of the reaction, the crude mixture was poured into 500 mL of methanol/hydrochloric acid mixture (20:1, v/v) for polymer precipitation, and the crude solid filter cake was collected by suction filtration. The filter cake was subjected to Soxhlet extraction with acetone as the extractant over three days. After extraction, the solid residue was dried in a vacuum oven at 30 °C for 12 h to afford the achiral polyfluorene derivative P3 (1.2 g) with a yield of approximately 59%.

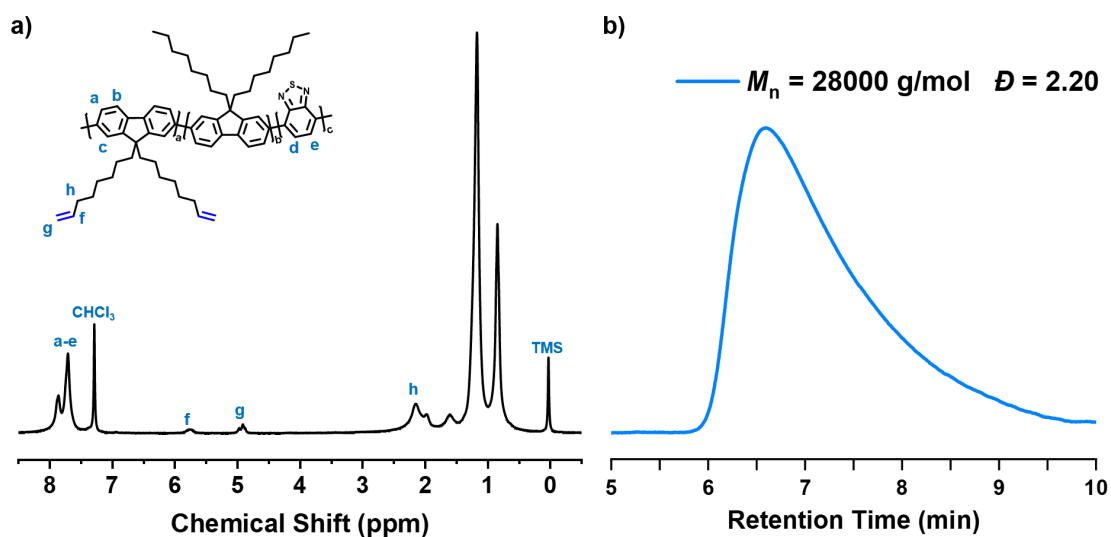
2. Supplementary Figures and Tables



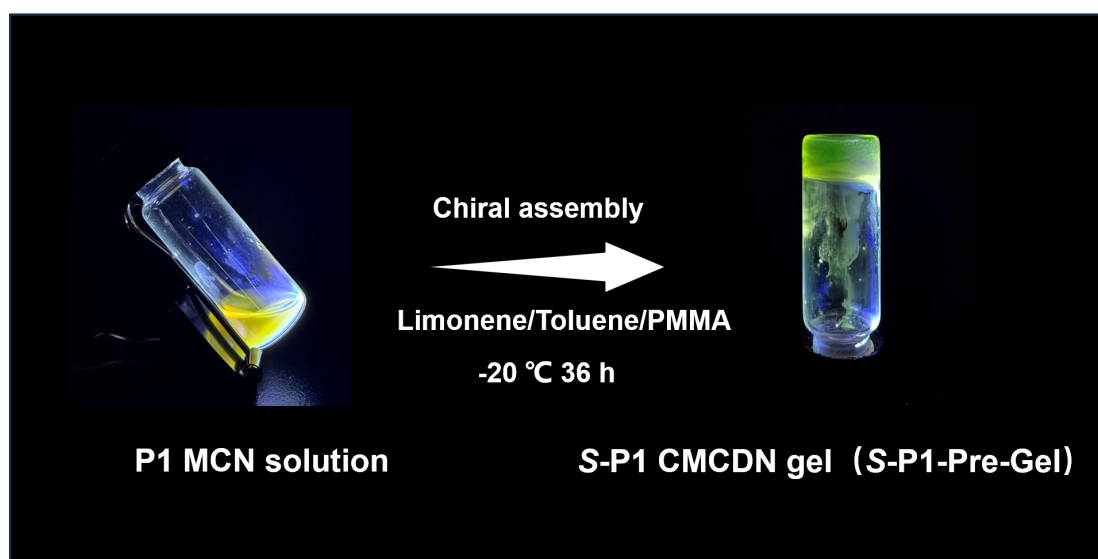
Supplementary Figure 1. Synthetic route for the monomer 2,7-dibromo-9,9-di(7-octenyl)fluorene (F-Octene) and polyfluorene derivatives (PFO-BT, noted as P1).



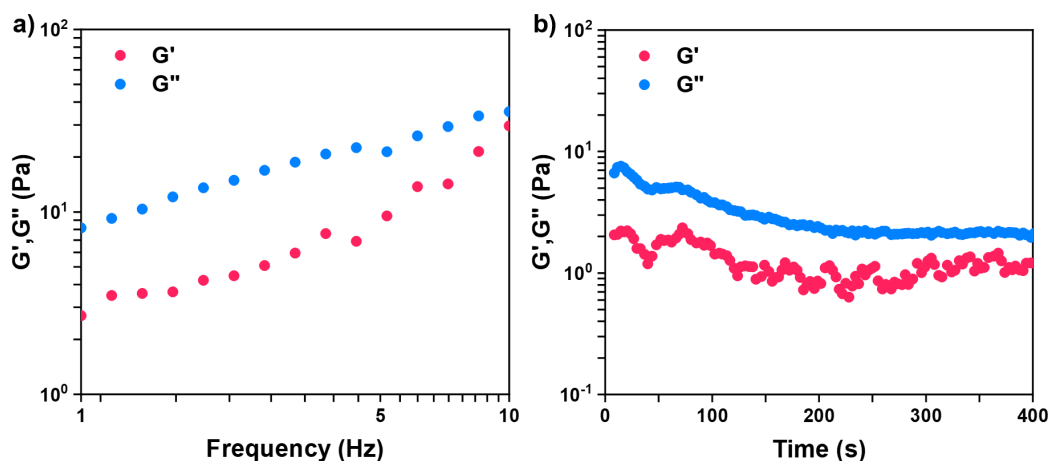
Supplementary Figure 2. ¹H NMR of the synthetic monomer F-Octene (CDCl₃): 7.61-7.34 (m, 6H), 5.92-5.59 (m, 2H), 5.11-4.73 (m, 4H), 2.03-1.79 (m, 8H), 1.43-0.80 (m, 16H).



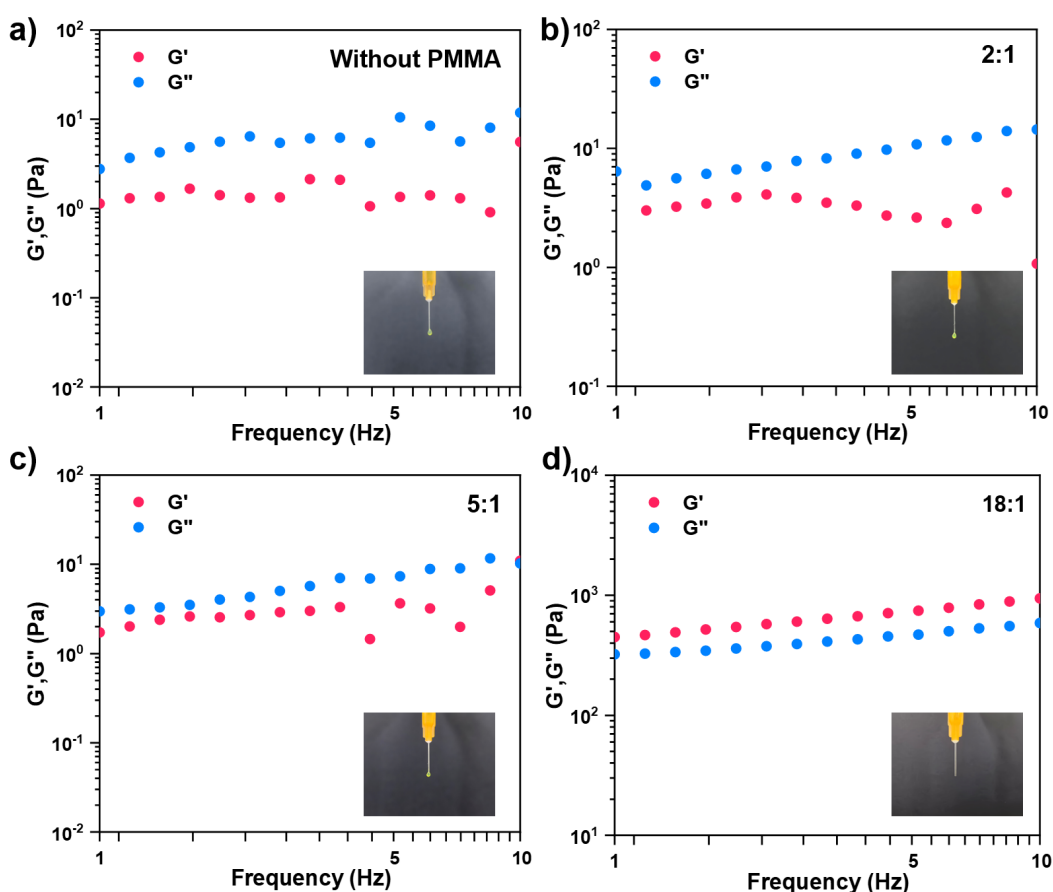
Supplementary Figure 3. (a) ^1H NMR of the synthetic polymer P1 (CDCl_3) and (b) GPC curve. The chemical shifts of representative hydrogen atoms are shown in the figure. The polymerization proportions of each section of a:b:c is 1:6.91:0.15, which is calculated by NMR data.



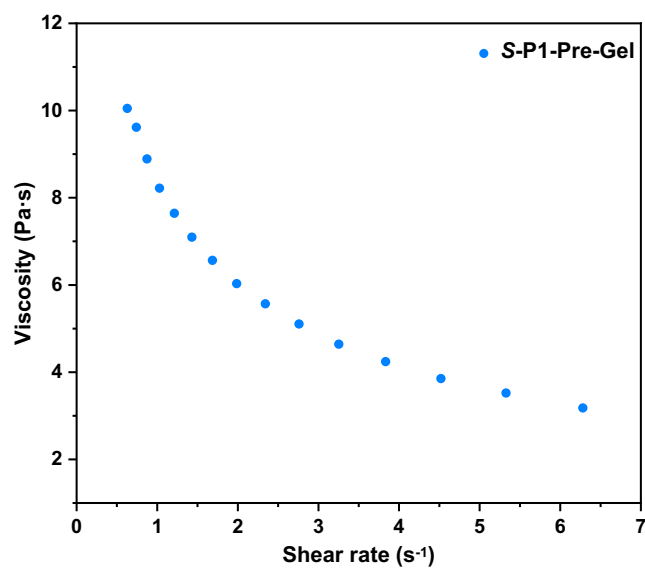
Supplementary Figure 4. Digital Photos of the gelation process of P1 MCN/S-limonene/toluene/PMMA system (noted as **S-P1-Pre-Gel**) from P1 MCN solution (Taking **S-P1-Pre-Gel** as an example).



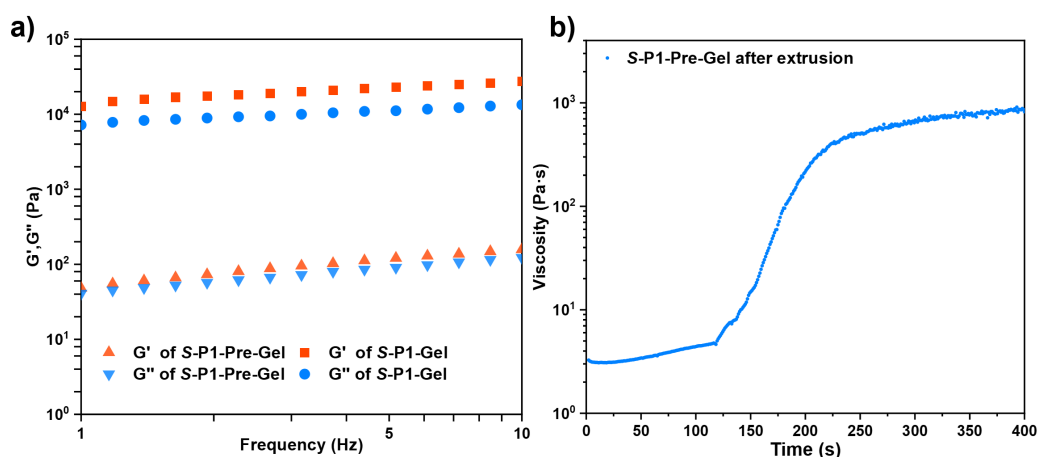
Supplementary Figure 5. The control experiment of S-limonene/PMMA system without P1. (a) Frequency sweep rheological test for S-limonene/PMMA system showing the solution state. (b) Rheological tests as a function of time of S-limonene/PMMA system after extrusion. Notes: Rheological tests were performed on gels formed by S-limonene as an example. Because rheological properties were independent of chirality.



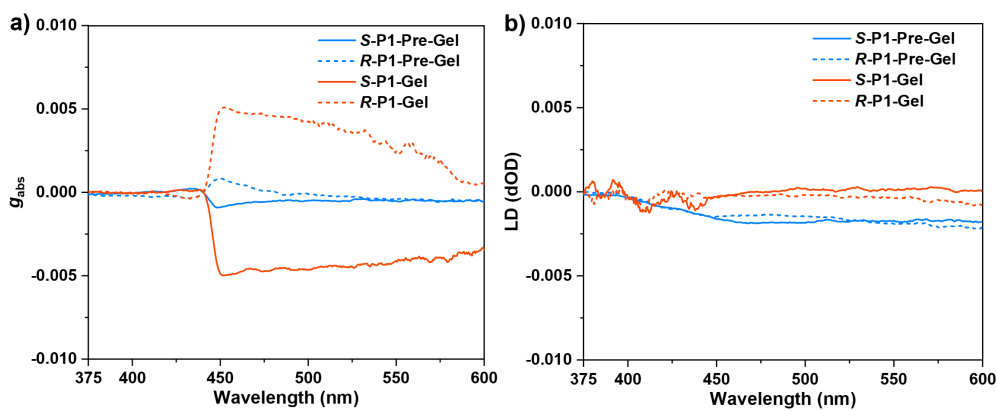
Supplementary Figure 6. The control experiment of preparing **S-P1-Pre-Gel** with different PMMA ratio. (a) Without PMMA. (b) The mass ratio of P1:PMMA is 2:1. (c) The mass ratio of P1:PMMA is 5:1. (d) The mass ratio of P1:PMMA is 18:1. The inset is the corresponding photograph of extrusion test of the different **S-P1-Pre-Gel**.



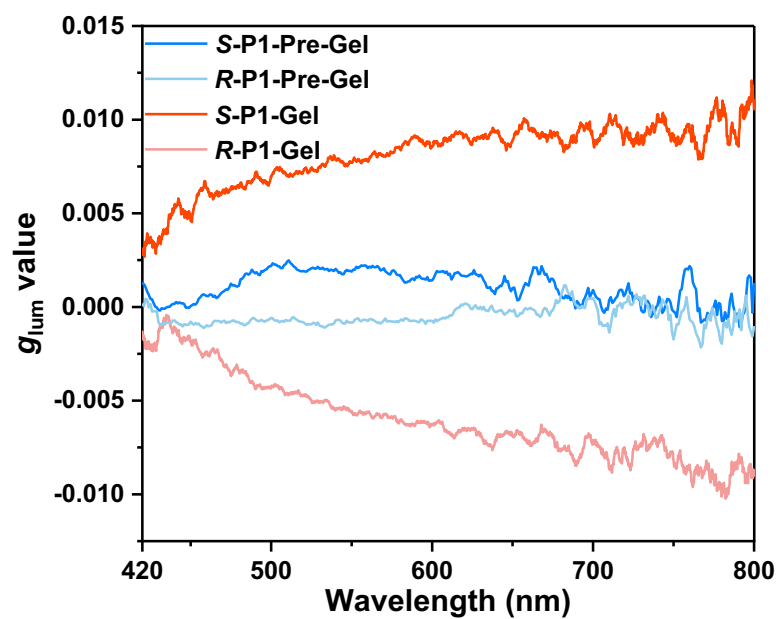
Supplementary Figure 7. S-P1-Pre-Gel viscosity as a function of shear rate.



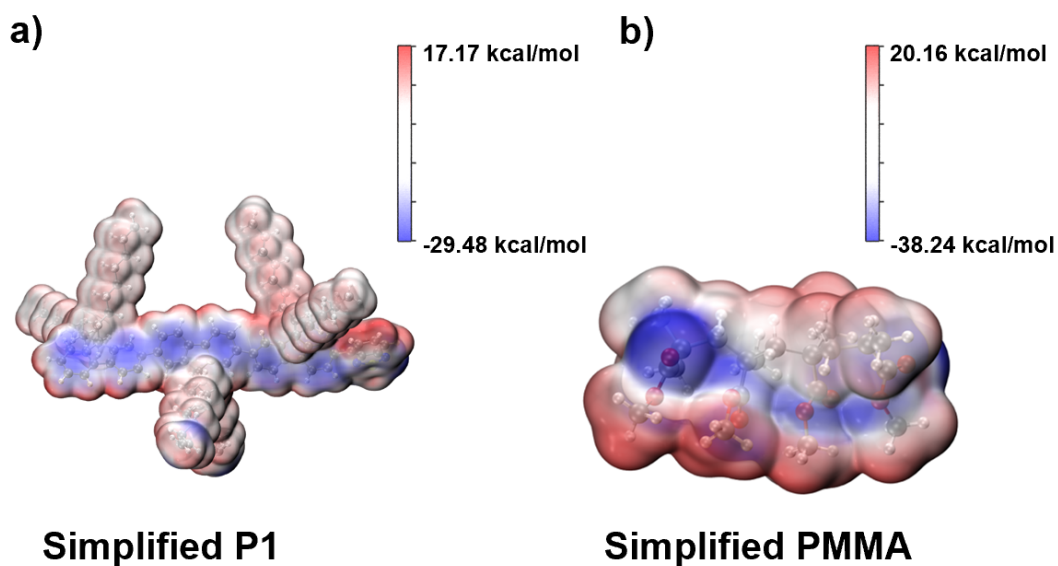
Supplementary Figure 8. (a) Rheological tests as a function of frequency of **S-P1-Pre-Gel** and **S-P1-Gel**, respectively. (b) **S-P1-Pre-Gel** viscosity after extrusion as a function of time.



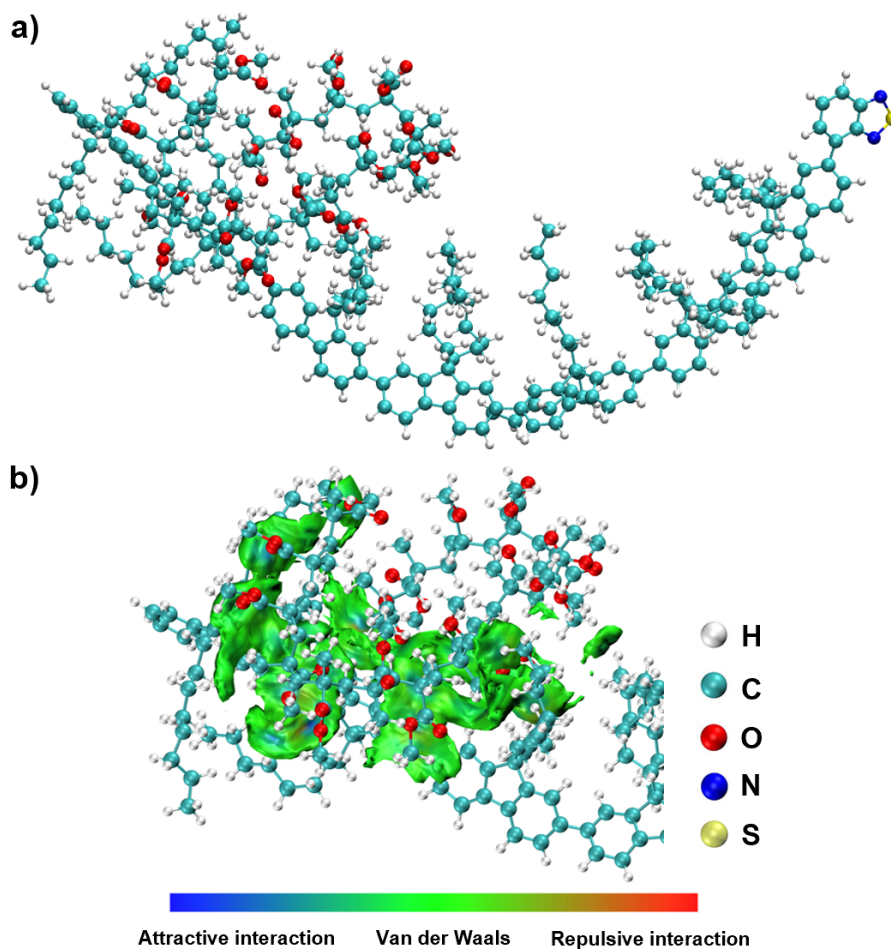
Supplementary Figure 9. g_{abs} values of P1 gel and LD spectra of **S/R-P1-Pre-Gel** and **S/R-P1-Gel**.



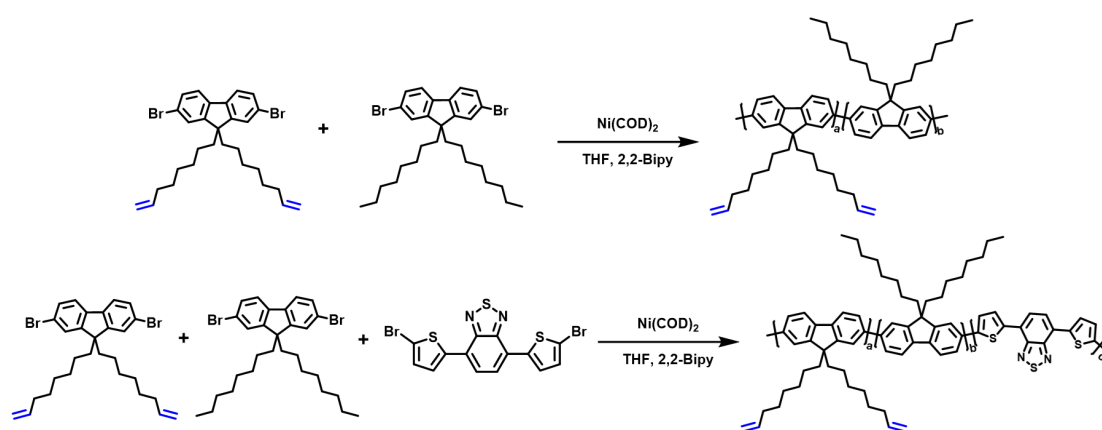
Supplementary Figure 10. g_{lum} value curves of S/R-P1-Pre-Gel and S/R-P1-Gel.



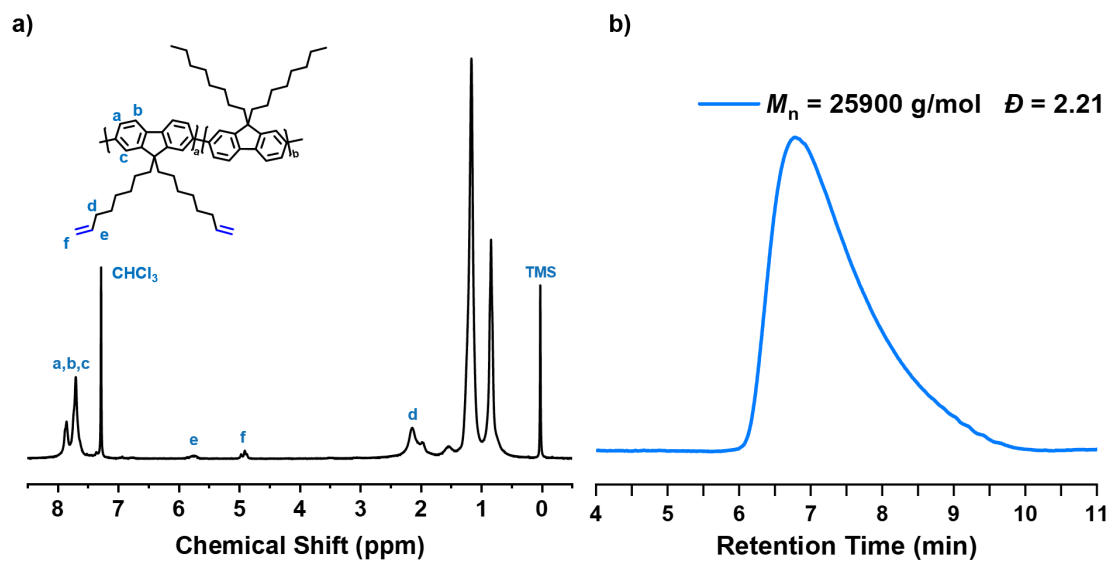
Supplementary Figure 11. The electrostatic potential (ESP) distribution of simplified P1 (a) and PMMA (b).



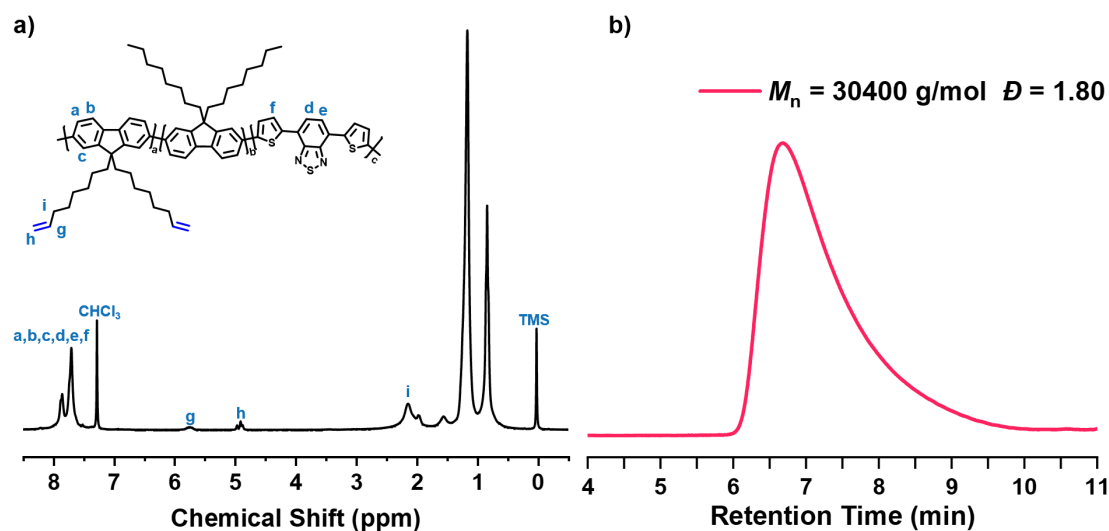
Supplementary Figure 12. (a) The optimized hybridized model between P1 and PMMA obtained by Forcite module of Materials Studio. (b) The modified independent gradient model (mIGM) based on Hirshfeld partition analysis oligomers visualizing the obvious van der Waals interactions between P1 and PMMA oligomers.



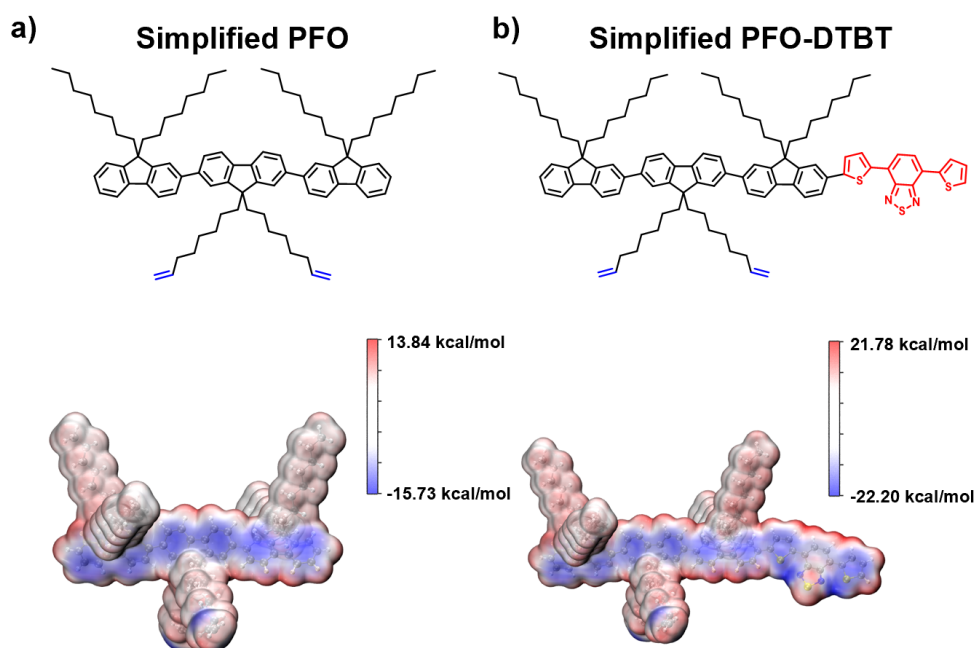
Supplementary Figure 13. Synthetic route for polyfluorene derivatives PFO (noted as P2) and PFO-DTBT (noted as P3).



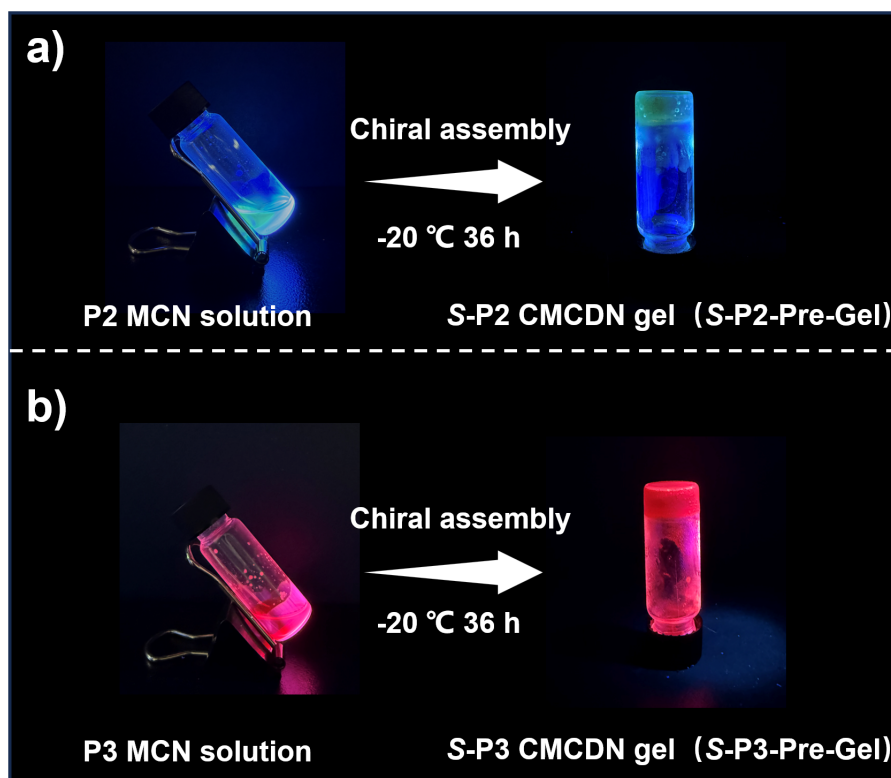
Supplementary Figure 14. (a) ^1H NMR of the synthetic polymer P2 (CDCl_3) and (b) GPC curve. The chemical shifts of representative hydrogen atoms are shown in the figure. The polymerization proportions of each section of a:b is 1:6.76, which is calculated by NMR data.



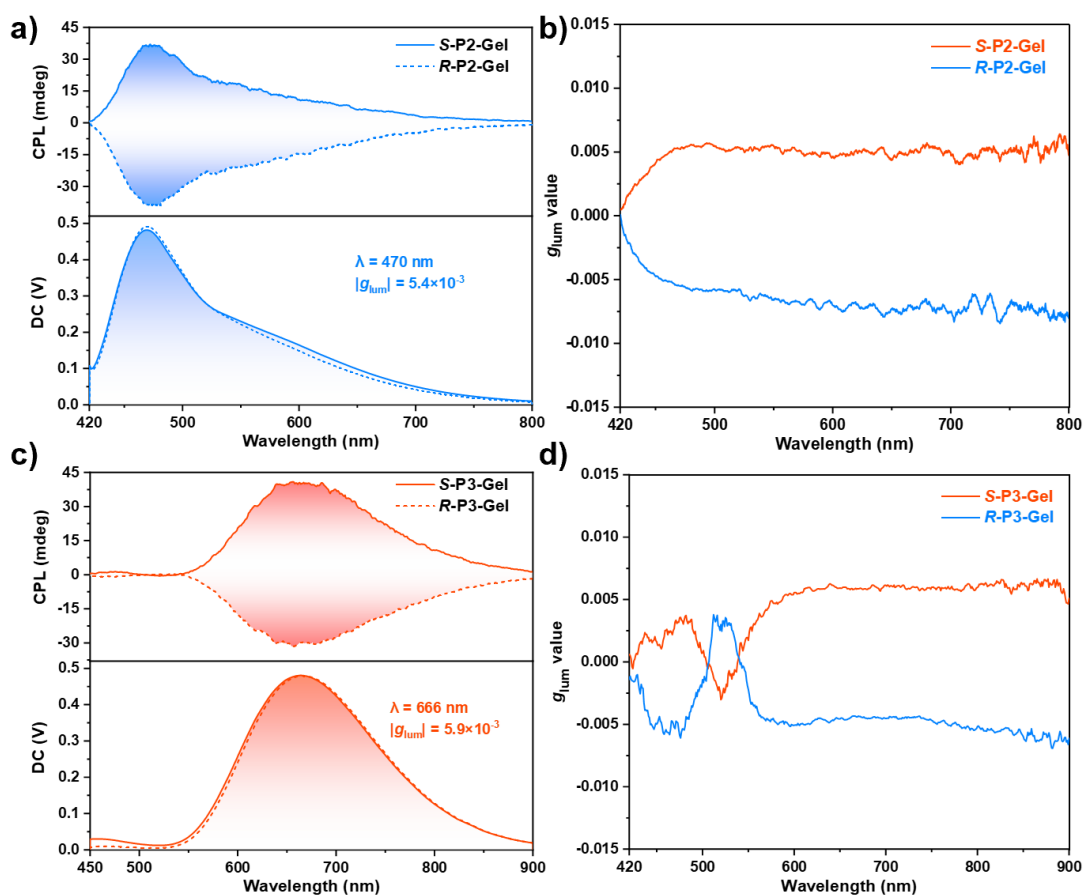
Supplementary Figure 15. (a) ^1H NMR of the synthetic polymer P3 (CDCl_3) and (b) GPC curve. The chemical shifts of representative hydrogen atoms are shown in the figure. The polymerization proportions of each section of a:b:c is 1:6.54:0.47, which is calculated by NMR data.



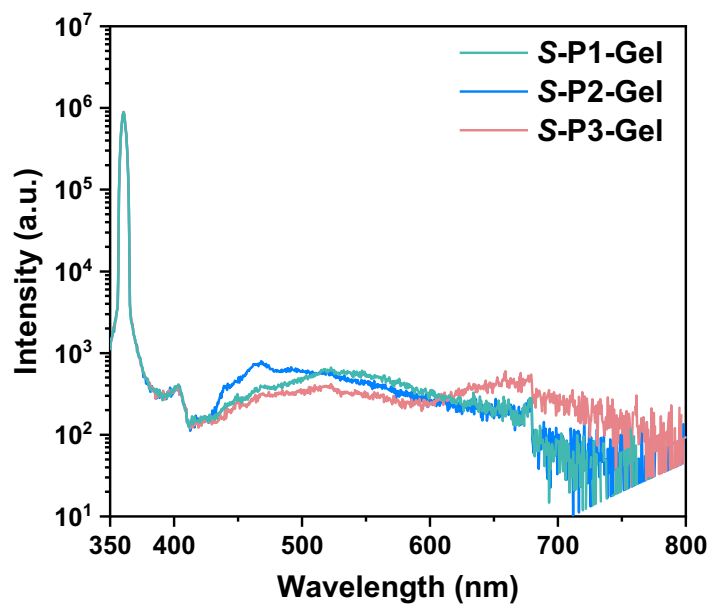
Supplementary Figure 16. The electrostatic potential on molecular surface of simplified PFO (P2) and PFO-DTBT (P3), respectively.



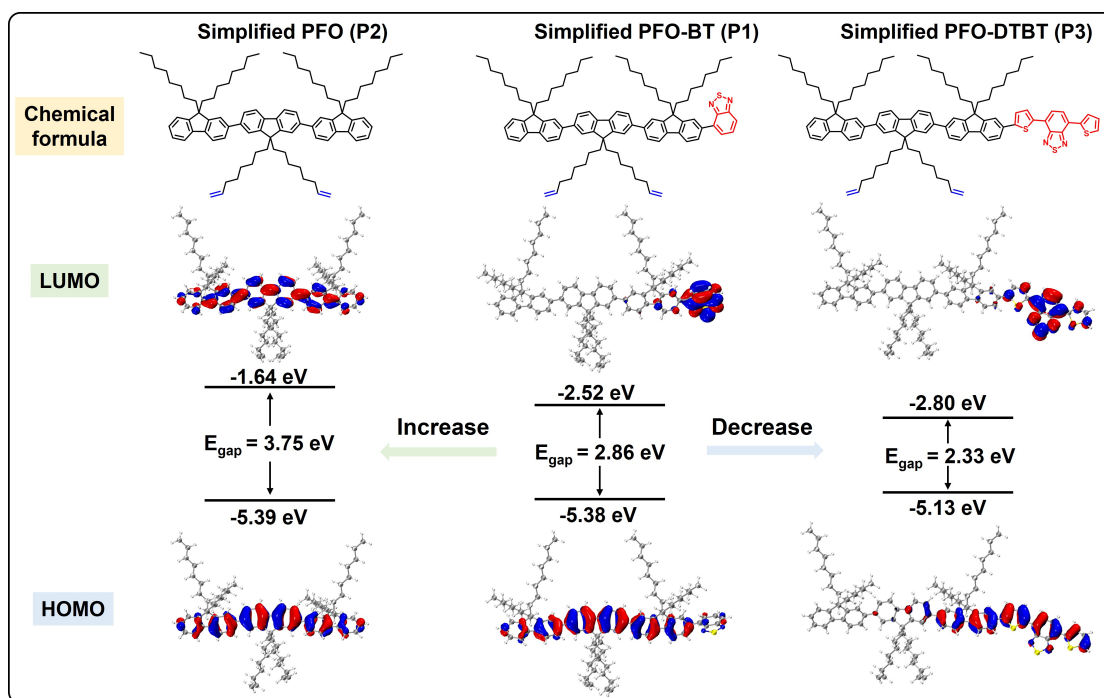
Supplementary Figure 17. (a) Digital photos for the preparation process of the P2 chiral CMCDN precursor gel (noted as **S-P2-Pre-Gel**) from P2 MCN solution by chiral assembly. (b) Digital photos for the preparation process of the P3 CMCDN precursor gel (noted as **S-P3-Pre-Gel**) from P3 MCN solution by chiral assembly.



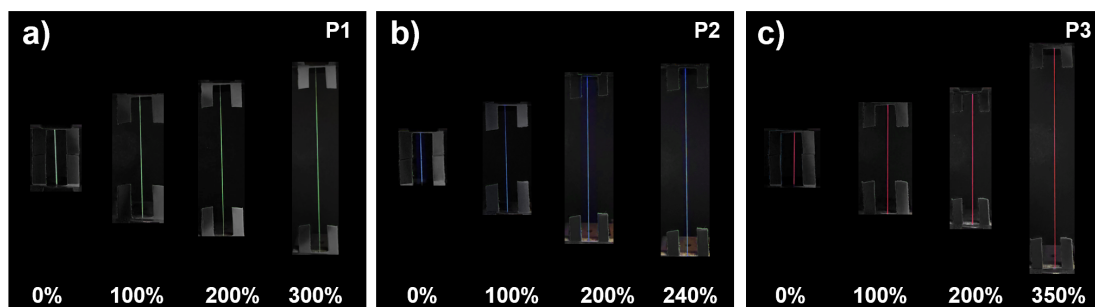
Supplementary Figure 18. (a) CPL spectra of **S/R-P2-Gel**. (b) g_{lum} value curve of **S/R-P2-Gel**. (c) CPL spectra of **S/R-P3-Gel**. (d) g_{lum} value curve of **S/R-P3-Gel**.



Supplementary Figure 19. Quantum yield (QY) measurement of **S-P1-Gel**, **S-P2-Gel**, and **S-P3-Gel**, respectively.



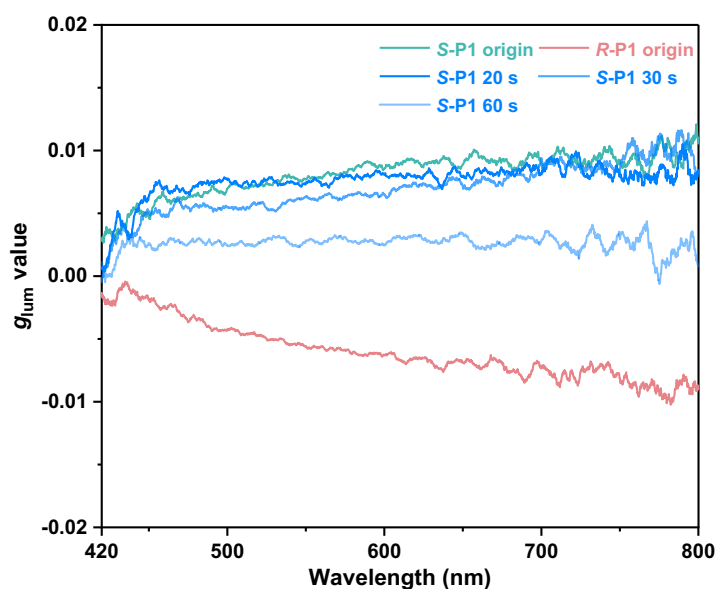
Supplementary Figure 20. Energy level diagram of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of simplified P1, P2 and P3 oligomers according to density function theory (DFT) calculations.



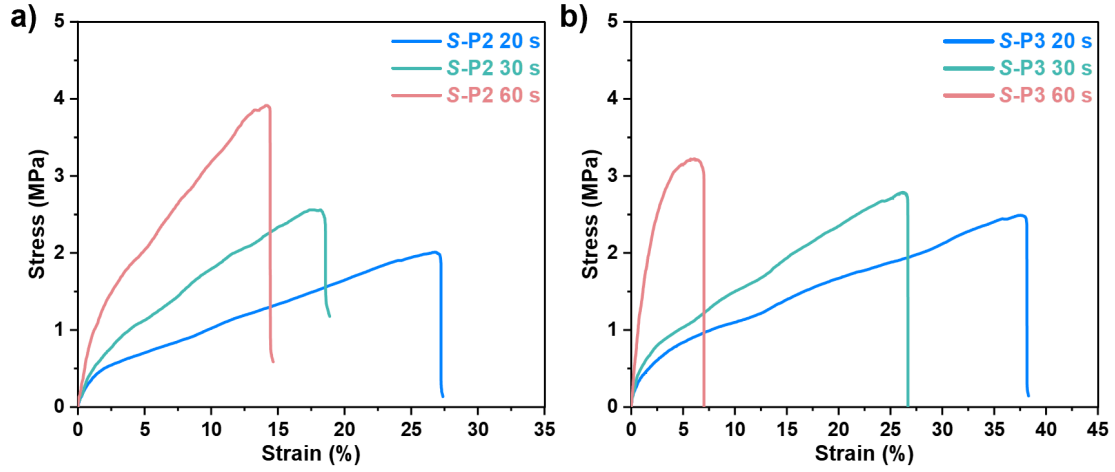
Supplementary Figure 21. Digital photographs of macroscopic stretch of different polymer gels (**S-P1-Gel**, **S-P2-Gel**, and **S-P3-Gel**) under UV light.

Supplementary Table 1. Comparison of mechanical and chiroptical properties of different gels with different secondary crosslinking times.

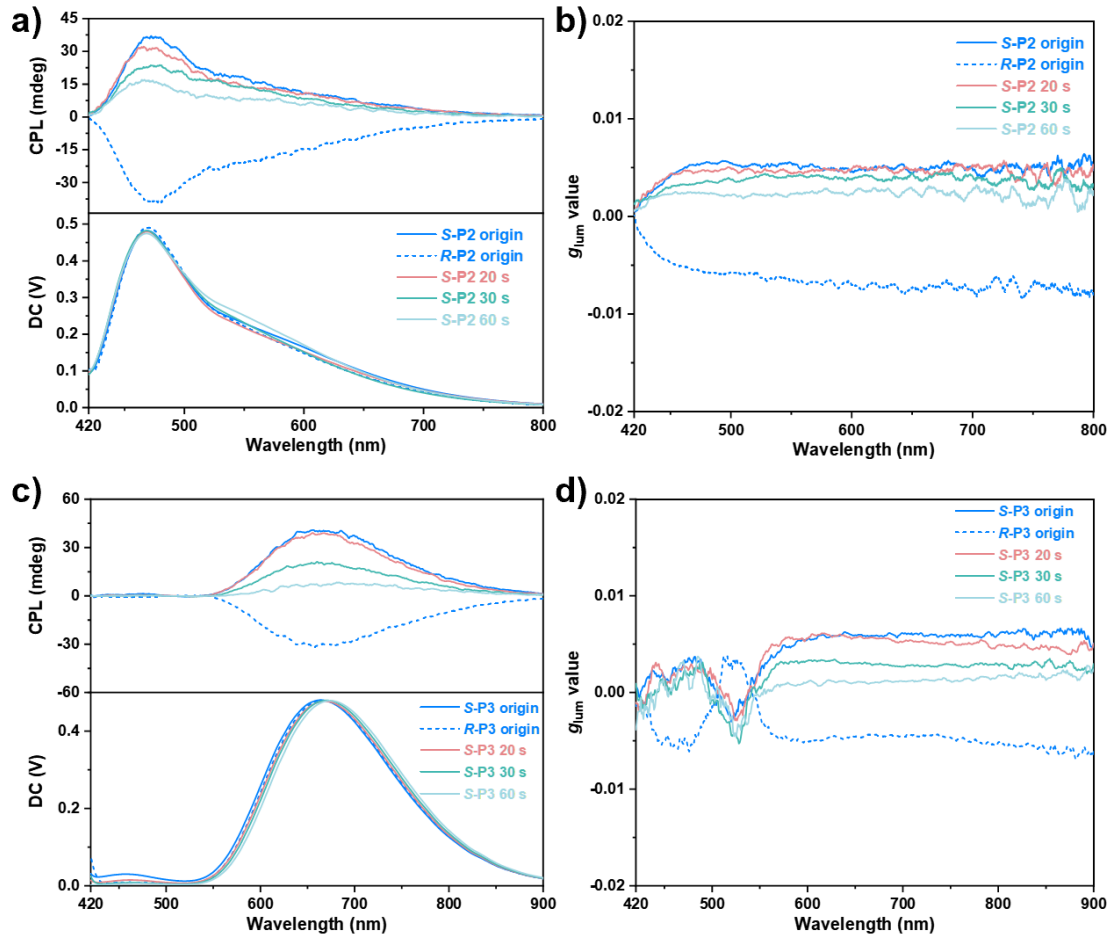
Gels	Crosslinking Time (s)	Tensile Strain (%)	Young's Modulus (MPa)	g_{lum} (10^{-3})
S-P1-Gel	0	317.89	0.78	7.6
	20	31.18	5.43	7.5
	30	14.57	13.5	6.3
	60	3.02	80.03	2.8
S-P2-Gel	0	245.16	0.85	5.3
	20	26.41	7.82	4.5
	30	17.73	12.63	3.3
	60	14.09	22.12	2.5
S-P3-Gel	0	351.31	0.87	5.9
	20	37.52	6.02	5.7
	30	26.47	9.63	3.0
	60	6.25	51.06	1.1



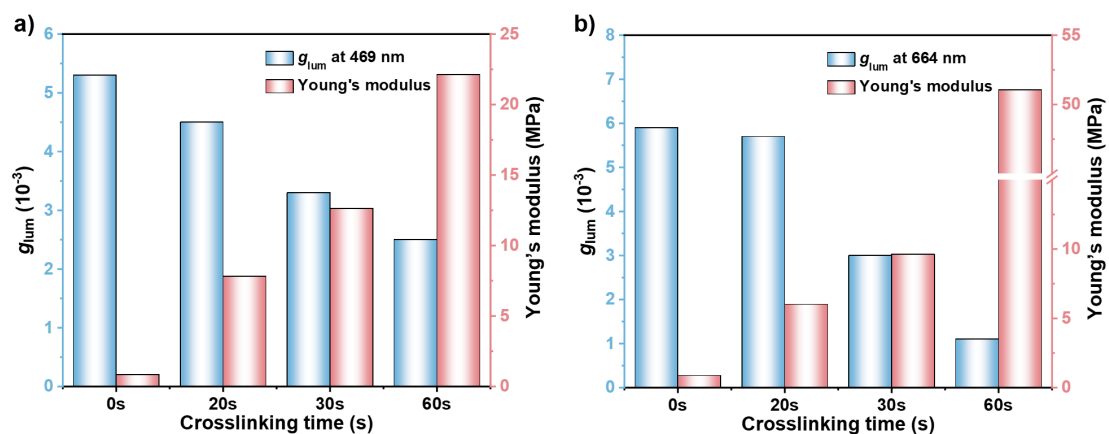
Supplementary Figure 22. The g_{lum} value curves of **S-P1-Gel** after crosslinking at different times (noted as S-P1 seconds for clarity).



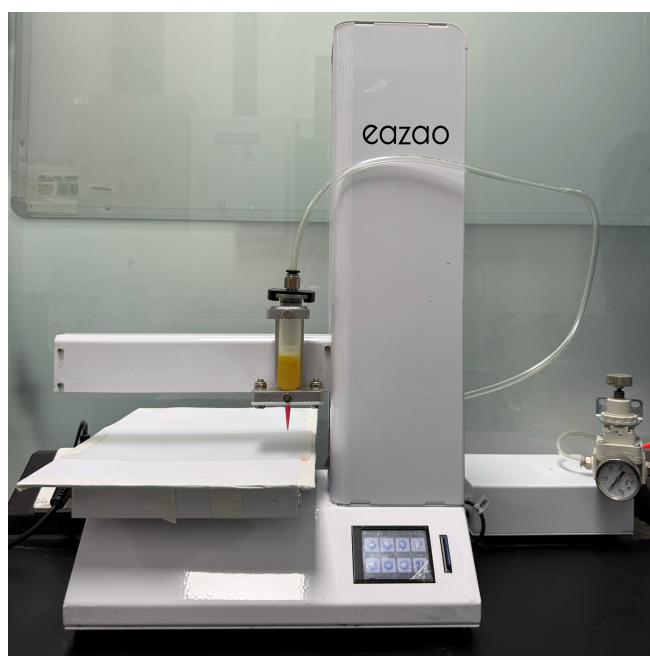
Supplementary Figure 23. (a) Stress-strain curves of **S-P2-Gel** with different crosslinking time. (a) Stress-strain curves of **S-P3-Gel** with different crosslinking time (noted as S-P2/3 seconds for clarity).



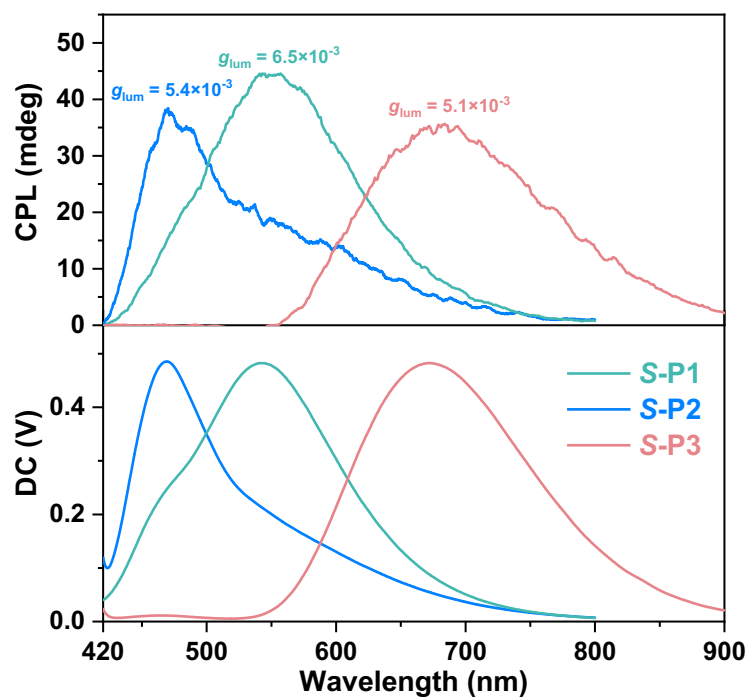
Supplementary Figure 24. CPL spectra (a) and g_{lum} value curves (b) of **S-P2-Gel** with different crosslinking time. CPL spectra (c) and g_{lum} value curves (d) of **S-P3-Gel** with different crosslinking time.



Supplementary Figure 25. (a) g_{lum} value at 469 nm and Young's modulus of **S-P2-Gel** with different crosslinking time. (b) g_{lum} value at 664 nm and Young's modulus of **S-P3-Gel** with different crosslinking time.



Supplementary Figure 26. The equipment photos of DIW type 3D printers manufactured by EAZAO from Hangzhou Regenovo Biotechnology Co. Ltd., China.



Supplementary Figure 27. CPL spectra of 3D printed gel models in three colors, respectively, showing the similar g_{lum} values with extrusion method.