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

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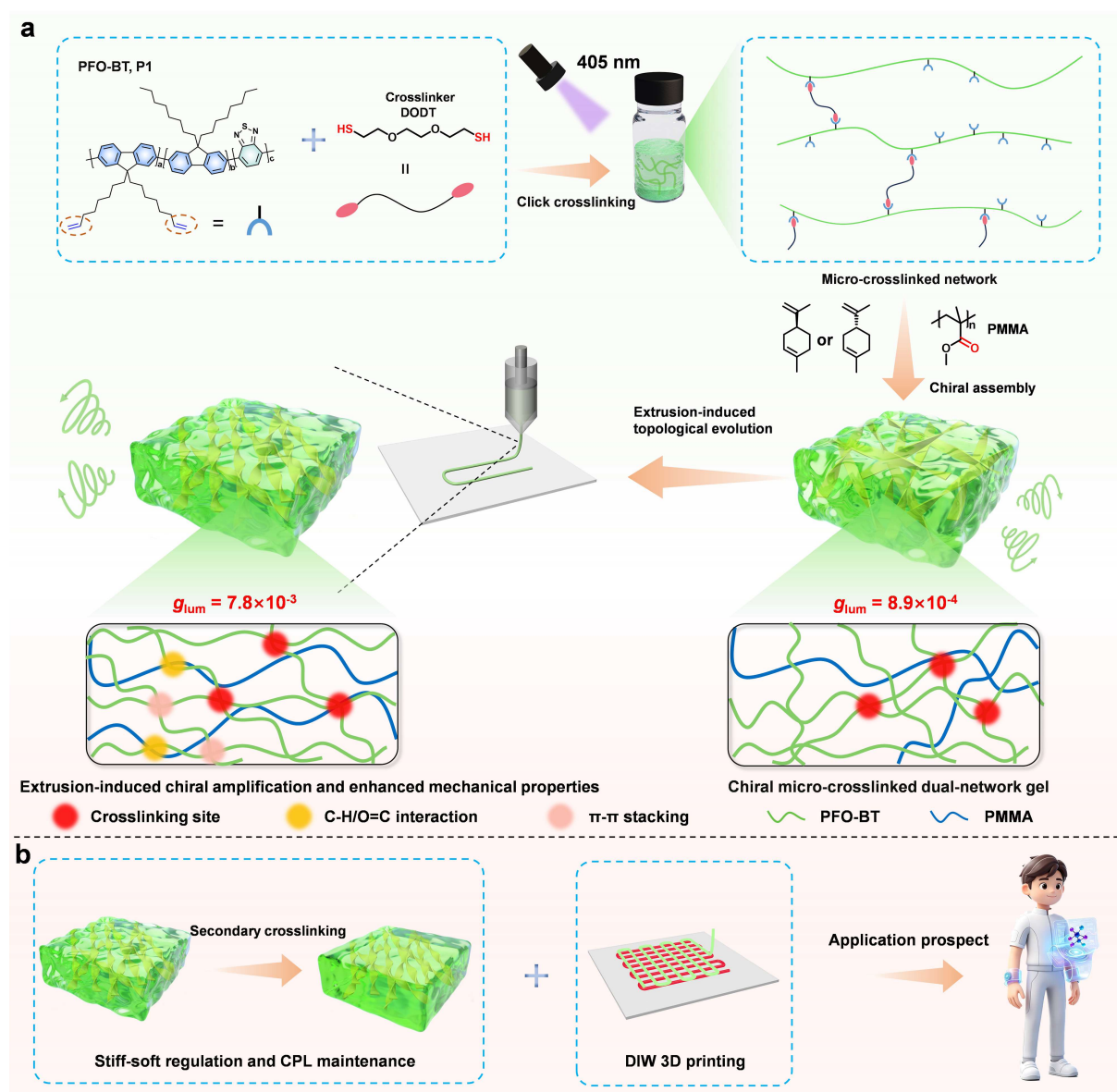
Abstract: Flexible circularly polarized luminescence (CPL) materials hold promise for solving the mechanical property mismatch between 3D-display wearable devices and continuously moving human tissues. However, the construction of flexible and processable CPL materials still remains challenging. Herein, we reported a strategy that leveraged chiral micro-crosslinked double-network (CMCDN) and extrusion-induced topological evolution (EITE) methods to construct flexible full-color CPL materials with tunable mechanics and directing 3D printability, which was enabled by synthetic fluorescent polyfluorene derivatives bearing side-chain crosslinking and chiral transfer sites. Through thiol-ene click reaction and chiral assembly, the extrudable precursor gel featuring CMCDN composed of polyfluorene derivatives and poly(methyl methacrylate) was prepared. Subsequently, upon syringe extrusion, the precursor gel underwent EITE, significantly improving mechanical properties and CPL intensity. Structural characterization demonstrated that shear-driven chain orientational rearrangement, partial crystallization, and multiple non-covalent interactions served as the primary governing factors for the performance enhancement. We extended the types of polyfluorene derivatives to achieve full-color stretchable CPL gels with considerable luminescence asymmetry factor. Secondary crosslinking can achieve rational regulation of their mechanical properties and CPL signals. Due to the excellent mechanical properties, by combining 3D printing technology, we successfully constructed a multi-layered, multicolor flexible CPL-active object without the aid of other auxiliary materials, guiding the way for the automated and large-scale manufacturing of flexible chiroptical devices.

1 Introduction

2 Circularly polarized luminescence (CPL) materials are indispensable for next-generation photonic
3 applications including 3D displays, optical communications, and information encryption¹⁻⁹. For instance, in
4 the field of 3D displays, compared with conventional technology, CPL can effectively enhance display
5 contrast and reduce visual distortion owing to its unique helical optical properties^{10,11}. Currently, the
6 extensively explored CPL-active materials mainly encompass liquid crystals, supramolecular assemblies,
7 polymers, and chiral inorganic materials, *etc*¹²⁻²⁶. Despite the unique strengths of each system, several
8 inherent limitations persist and restrict their practical application. For example, cholesteric liquid crystals
9 afford large luminescence dissymmetry factors (g_{lum}) over 0.1, while their inherent fluidity generally
10 demands encapsulation within cavity architectures²⁷⁻³¹. Supramolecular assemblies generally enable
11 dynamically tunable CPL responses through non-covalent interactions³²⁻³⁵, yet their spontaneous
12 formation in solution or films imposes severe constraints on processing and molding. Driven by the rapid
13 progress of high-performance wearable 3D-display devices, the flexibility and processability of CPL
14 materials with large g_{lum} play a vital role in attaining seamless integration with dynamically moving
15 biological tissues. However, the preparation of flexible and processable CPL materials still faces a
16 significant challenge.

17 Gels consist of solvent-swollen crosslinked polymer networks, which serve as versatile soft functional
18 materials for flexible electronics, soft devices and biomedicine due to their inherent flexibility, adjustable
19 network architectures and good processability³⁶⁻⁴². Among a wide variety of gel materials, the extrudable
20 gels feature unique processing advantages given their shear-thinning behavior that enables smooth
21 extrusion through syringes or printing nozzles under shear and their rapid post-shear sol-gel transition that
22 renders extruded geometries self-supporting⁴³⁻⁴⁶. Importantly, for chiral gels, extrusion-driven chain
23 alignment permits in-situ tuning of molecular stacking and supramolecular chirality, matching the structural
24 demands of chiroptical materials⁴⁷. Additionally, extrudable gels can also be used as extrusion-based 3D-
25 printing ink, representing promising soft advanced materials⁴⁸. However, the currently reported CPL-active
26 gels were formed through supramolecular interactions driven by weak non-covalent bonds⁴⁹, which makes
27 it difficult to balance the gel fluidity during extrusion, post-extrusion shape retention, and chirality
28 preservation. How to construct highly ordered chiral microstructures in gels while maintaining extrusion
29 flowability and shape fidelity constitutes a core challenge that urgently needs to be addressed. Thus, it

1 remains a formidable task to construct high-performance extrudable CPL-active gels towards automated
 2 3D-printing processing.



3
 4 **Fig. 1 Schematic illustration of the preparation process of polymer-based flexible full-color CPL materials and 3D**
 5 **printing.** (a) Schematic illustration of the facile strategy for the formation of the chiral polymer gel exhibiting intense CPL
 6 and mechanical properties. The process mainly consists of three steps: the preparation of micro-crosslinking polymer
 7 solution, the formation of double-network precursor gel by chiral co-assembly, extrusion-induced topological evolution (EITE)
 8 of the precursor gel for chiral amplification and enhanced mechanical properties. (b) Schematic illustration of mechanical
 9 regulation by secondary crosslinking, direct ink writing (DIW) 3D printing and potential application prospect.

10 Herein, a synergistic strategy involving multi-step chemical and physical interactions is proposed to
 11 address the challenge. Firstly, we designed and synthesized a novel polyfluorene derivative featuring
 12 double bonds crosslinkable sites in the side chains. Then an extrudable chiral CPL precursor gel was
 13 constructed using a two-step method involving click reaction for micro-crosslinking and following chiral co-

assembly of a polymethyl methacrylate (PMMA)-based double polymer network with *S/R*-limonene. Extrusion via syringe further facilitated topological evolution of the polymer network, amplifying both the chirality and mechanical properties of the gels, due to the orientational rearrangement of the polymer chain structure and multiple non-covalent interactions including van der Waals forces, C-H/O=C and π - π stacking (**Fig. 1a**). Furthermore, similar polyfluorene derivatives with different electron-withdrawing groups in the main chain were synthesized, also achieving enhanced chirality and mechanical properties, enabling full-color CPL emission, which demonstrated the universality of this strategy. These gels exhibited excellent tensile properties and secondary crosslinking ability, enabling rational control of CPL and mechanical properties. Due to the excellent mechanical properties, the obtained precursor gel can be directly used for direct ink writing (DIW) 3D printing without additional auxiliary materials, and the printed model can achieve self-support, flexibility and chiral retention. Therefore, this work not only realizes the facile preparation and processing-shaping of flexible CPL materials, but also holds important application prospects in cutting-edge fields such as flexible chiroptical devices (**Fig. 1b**).

Results

Polymer synthesis and preparation of the precursor gel with chiral micro-crosslinked double-network (CMCDN)

Firstly, a typical achiral polyfluorene derivative was designed and synthesized by Yamamoto coupling reaction, using 2,7-dibromo-9,9-di(oct-7-en-1-yl)-9*H*-fluorene (monomer 1, abbreviated as F-Octene), 2,7-dibromo-9,9-dioctyl-9*H*-fluorene (monomer 2), and 4,7-dibromo-2,1,3-benzothiadiazole (monomer 3) as comonomers, as well as bis(1,5-cyclooctadiene)nickel(0) (Ni(COD)₂) as the catalyst (**Supplementary Fig. 1**). After the monomer 1 (F-Octene) was synthesized (**Supplementary Fig. 2**), the random polymer, PF8-*r*-F-Octene-*r*-BT (abbreviated as PFO-BT, noted as P1) was successfully synthesized by copolymerization of these achiral monomers, demonstrated by nuclear magnetic resonance (NMR) measurements and gel permeation chromatography (GPC) (**Supplementary Fig. 3**). As shown in **Supplementary Fig. 3b**, the molecular weight (M_n) of P1 was 28,000 g mol⁻¹ with the corresponding molecular weight distribution ($\mathcal{D}$) of 2.20. The polymerization proportion calculated by NMR data of monomer 1:monomer 2:monomer 3 was 1:6.91:0.15.

Subsequently, as presented in **Figs. 1a** and **2a**, using 2,2-dimethoxy-2-phenylacetophenone (abbreviated as DMPA) as a photo-initiator and toluene as a solvent, a micro-crosslinking reaction was

carried out under 405 nm light irradiation, through the double bond sites of the polymer side chains and the added dithiol crosslinking agent (2,2'-(ethane-(1,2-diylbis(oxy))) bis(ethane-1-thiol), abbreviated as DODT). NMR data before and after the reaction confirmed the occurrence of the thiol-ene click reaction (**Fig. 2b**). The conversion of double bonds was determined to be approximately 30% from the integration ratio of terminal olefin proton signals at positions f and g relative to the aromatic proton peak area as an internal reference. Excessive crosslinking may affect the subsequent chiral transfer, and the remaining double bonds will be used for secondary crosslinking of the gels to adjust their mechanical properties. Fourier transform infrared (FT-IR) spectroscopy further verified the completeness of the click reaction. As shown in **Fig. 2c**, a characteristic peak attributable to the sp^2 hybridization stretching vibration of the carbon-hydrogen ($-C=C-H$) bond at 3022 cm^{-1} was observed. Another characteristic peak change attributable to the stretching vibration of the $-C=C-$ bond at 1604 cm^{-1} also appeared. These characteristic peaks intensity decreased after crosslinking, indicating that the double bonds of the polymer side chains were partially reacted. To systematically investigate the regulatory effect of the click reaction on the chemical structure of the polymer, X-ray photoelectron spectroscopy (XPS) technology was used to analyze the evolution of the sulfur chemical environment in P1. As depicted in **Fig. 2d**, three characteristic binding energy peaks appeared in the narrow S 2p spectrum after the click reaction. The binding energy peak at 166.2 eV was attributed to the formation of C-S-C covalent bonds, confirming the efficient reaction between the double bond and the thiol group. The typical double peak structure at 164.9 eV and 163.7 eV was attributed to the spin orbital splitting of the thiol ($-SH$), indicating the presence of unreacted thiols in the system. Therefore, combining the integral data of the characteristic peaks in the NMR, FT-IR spectrum, and XPS, the crosslinked structure occupied a small part of the entire polymer system, successfully constructing a micro-crosslinked network (MCN) structure with limited crosslinking sites (**Figs. 1a and 2a**).

As shown in **Fig. 1a**, following the formation of the P1 micro-crosslinked structure, by introducing the second polymer PMMA and chiral inducer *S/R*-limonene, we further prepared chiral micro-crosslinked double-network (CMCDN) precursor gels (noted as ***S/R*-P1-Pre-Gel**) based on chiral assembly (**Fig. 1e and Supplementary Fig. 4**). As previously reported^{16,23,50}, *S/R*-limonene can act as a chiral source to transfer molecular chirality to polymer chains, and further drive the formation of chiral supramolecular assemblies. Meanwhile, PMMA, as the second type of polymer chain introduced into the system, enhanced the viscoelasticity of gel through non-covalent interactions and physical entanglement to form a dual network structure, thereby achieving its extrusion capability. After optimizing the proportions of different

1 components, we found that a PMMA to P1 mass ratio of 10:1 resulted in a gel with good extrusion
 2 properties (**Fig. 1e** and **the inset**). Extrudable gels cannot be formed without P1 or PMMA, or with
 3 inappropriate proportions (**Supplementary Figs. 5** and **6**). As shown in **Supplementary Fig. 4**,
 4 macroscopic inverted vial experiments confirmed the formation of **S-P1-Pre-Gel** and exhibited bright green
 5 fluorescence under 365 nm ultraviolet (UV) light. Rheological results further confirmed the formation of the
 6 viscoelastic gel, since the storage modulus G' was greater than the loss modulus G'' (**Fig. 1e**). In addition,
 7 the viscosity of the **S-P1-Pre-Gel** decreased as the shear rate increased, thus exhibiting shear-thinning
 8 characteristics (**Supplementary Fig. 7**). Circular dichroism (CD) spectra of **S/R-P1-Pre-Gel** exhibited
 9 mirror-image cotton effects, indicating the formation of chiral gels (**Fig. 1f**). In addition, CPL spectra of **S/R-**
 10 **P1-Pre-Gel** displayed a detectable CPL signal intensity with the g_{lum} of 8.9×10^{-4} ($\lambda_{max} = 471$ nm) (**Fig. 2g**).

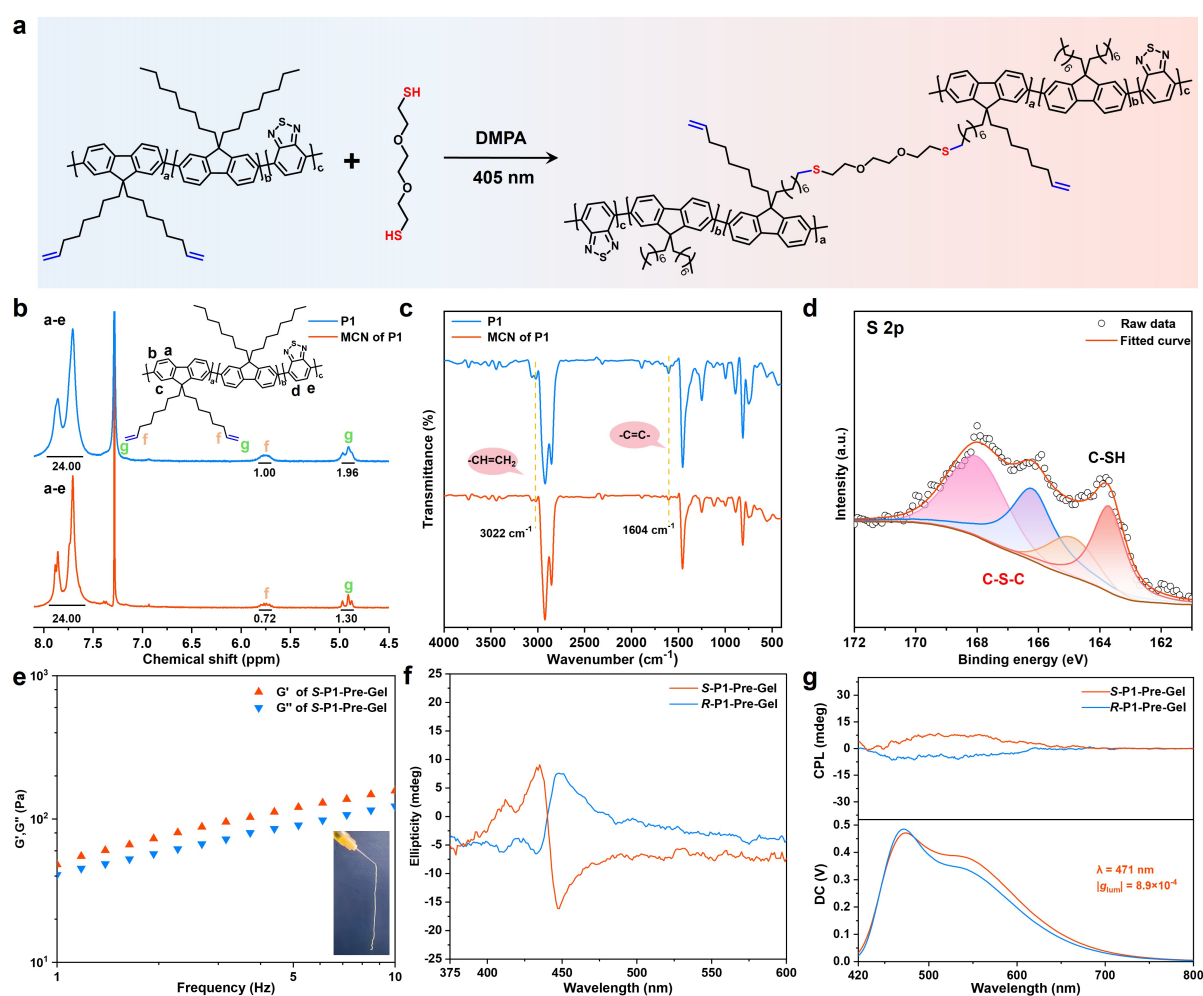


Fig. 2 The formation process of chiral precursor gel with CMCDN structure of P1. (a) Chemical reaction formula of polymer crosslinking via thiol-ene click reaction. (b) NMR and (c) FT-IR spectra of P1 before and after chemical crosslinking. (d) XPS spectra of P1 after chemical crosslinking. (e) Rheological test of S-P1 CMCDN precursor gel (noted as S-P1-Pre-Gel). The inset is the photograph for the extrusion capability test of S-P1-Pre-Gel. (f) CD spectra of S/R-P1-Pre-Gel. (g) CPL spectra of S/R-P1-Pre-Gel. (Notes: Rheological tests were performed on gels induced by S-limonene as an example.)

Extrusion-induced topological evolution (EITE) for preparing robust chiral gels with intense CPL

After extrusion process, a self-reinforcing gel that exhibited a stronger chiral signal and enhanced mechanical properties was obtained (**Figs. 1a and 3**). As shown in **Fig. 3a**, the schematic diagram illustrated two process that occurred after the extrusion of **S/R-P1-Pre-Gel**: shear-thinning to initial solution state and further EITE to steady state. Time-dependent rheological curves demonstrated the secondary gelation and evolution process after extrusion, in which the initial liquid state transformed into a gel state (sol-gel transition) at approximately 120 s (**Fig. 3b**). At 350 seconds, the gel reached a stable structure (noted as **S/R-P1-Gel**). Notably, **S-P1-Gel** exhibited G' and G'' that were 100 times higher than those of **S-P1-Pre-Gel** (**Fig. 3b** and **Supplementary Fig. 8a**), with the steady-state viscosity reaching 1000 Pa · s (**Supplementary Fig. 8b**), confirming significantly improved mechanical properties. Fluorescence (FL) and CPL dynamic spectra tests (**Figs. 3c and 3d**) were conducted to monitor changes in gel structure after extrusion. As shown in **Fig. 3c**, after extrusion the sol-gel transition process was accompanied by a change in the color of the fluorescent emission, gradually changing from blue-green to green, indicating a change in the internal structure of the gel. Dynamic CPL spectra (**Fig. 3d**) indicated a changed process during which the chiral signal disappeared, gradually increased, and then stabilized. **Figs. 3e and 3f** showed the chiral structural information of **S/R-P1-Gel**. Mirror-image CD and CPL signals can be observed through S/R-limonene induction with different molecular chirality. The results revealed that both of the gels before and after extrusion were chiral, but the extruded **S/R-P1-Gel** exhibited a significant enhancement in chiral signaling including g_{abs} and g_{lum} (**Supplementary Figs. 9a and 10**). Linear dichroism (LD) spectra indicated that LD contributed very little to the detected CD signals (**Supplementary Fig. 9b**). The **S-P1-Gel** exhibited a considerable g_{lum} of 7.8×10^{-3} ($\lambda_{\text{max}} = 551 \text{ nm}$) for polymer-based soft materials, which was 8.8-fold higher than that of **S-P1-Pre-Gel**.

Then, we analyzed the interactions between the two polymers using theoretical calculations to get deeper insights into the dual-polymer network. The electrostatic potential (ESP) distribution of simplified P1 and PMMA structures was plotted (**Supplementary Fig. 11**). The P1 polymer backbone exhibited a negative ESP, while the PMMA side chain ends exhibited a strong positive ESP, demonstrating the possibility of electrostatic interaction between the two polymers. Furthermore, the modified independent gradient model (mIGM) calculation was carried to analyze the specific interactions between the two polymers. Two oligomer models containing eight monomers were constructed to simulate the internal structure of the extruded gel in the lowest-energy state (**Supplementary Fig. 12a**). The green isosurface

represented van der Waals interactions (**Fig. 3g** and **Supplementary Fig. 12b**). In addition, the C-H/O=C interaction with the distance of 2.39 Å between the ester bonds of the PMMA and the alkyl side chains of P1 was clearly observed and exhibited stronger attraction in blue color than van der Waals interactions⁵¹. Therefore, it can be speculated that the shear force during extrusion may induce stronger attractive forces between polymers, thereby leading to improved gel mechanical properties.

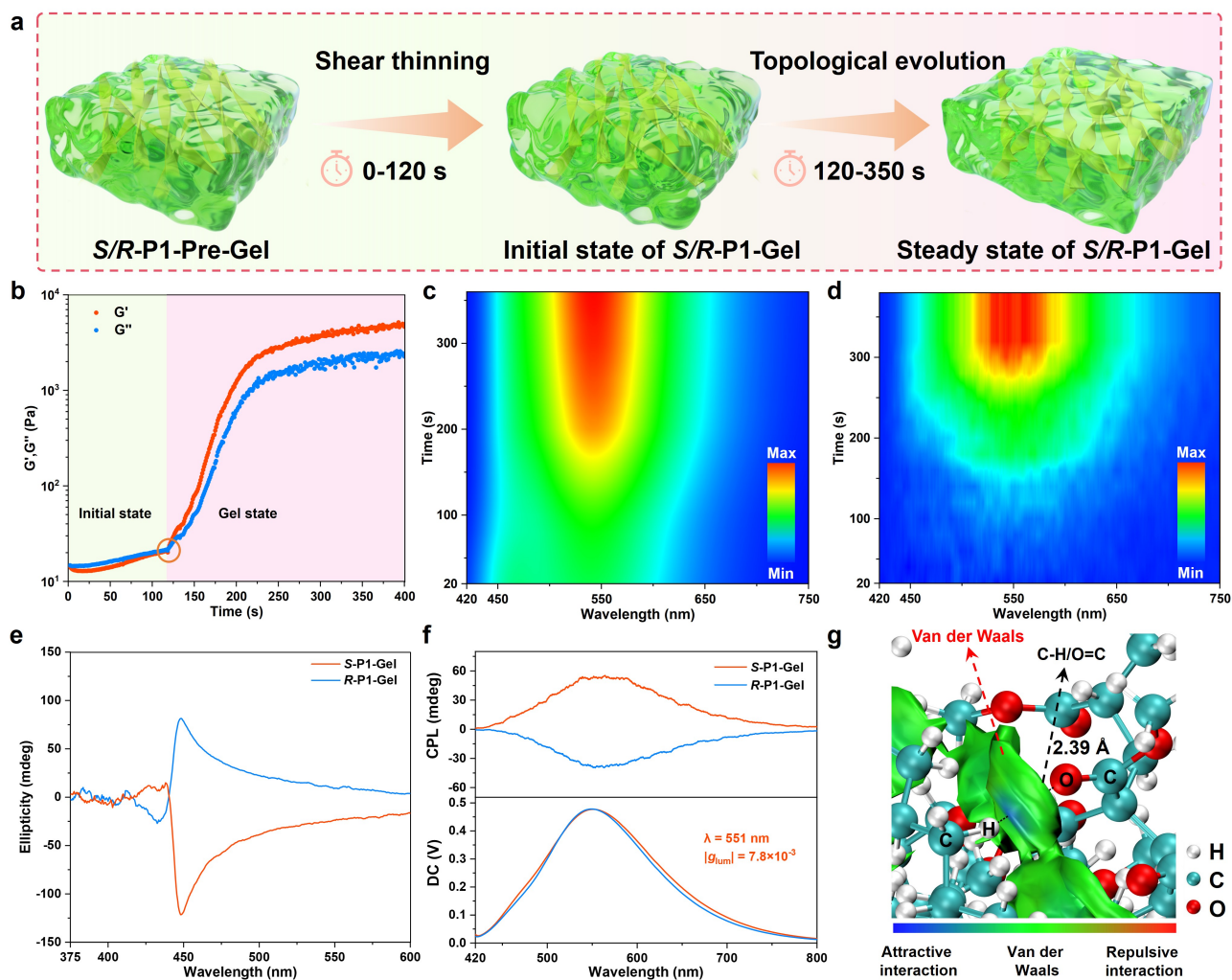


Fig. 3 The preparation of robust and improved CPL-active S/R-P1-Gel by extrusion-induced topological evolution (EITE). (a) Schematic diagram illustrating EITE process for preparing robust polymer gels with intense CPL. (b) Rheological curves of S-P1-Pre-Gel at different times after extrusion. (c) 2D FL spectra of S-P1-Pre-Gel at different times after extrusion. (d) 2D CPL spectra of S-P1-Pre-Gel at different times after extrusion. (e) CD spectra of S/R-P1-Gel. (f) CPL spectra of S/R-P1-Gel. (g) The mIGM calculation for the interactions between P1 and PMMA oligomer chains.

Furthermore, to explore the mechanism of chiral amplification in the EITE process, two-dimensional grazing-incidence wide-angle X-ray scattering (2D GIWAXS) and polarized optical microscopy (POM) experiments were carried out on the **S-P1-Pre-Gel** and **S-P1-Gel**. As shown in **Figs. 4a** and **4b**, the two gels showed two distinct patterns. The **S-P1-Pre-Gel** exhibited a relatively weak signal intensity, while the

diffraction signal peak of **S-P1-Gel** including (100) and (010) peaks was significantly enhanced. The normalized intensity distribution of the signal in the q range of 1.0-1.1 $\text{\AA}^{-1}$ as a function of the azimuth angle (χ) was obtained (**Fig. 4c**). The results indicated that both of them contained edge-on and face-on packing structures. But the two structures were present in different proportions in the two types of gels. In **S-P1-Pre-Gel**, the two account for almost the same proportion, exhibiting a disordered structure. In **S-P1-Gel**, the proportion of face-on region was significantly higher than that of edge-on, indicating a certain degree of orientational arrangement.

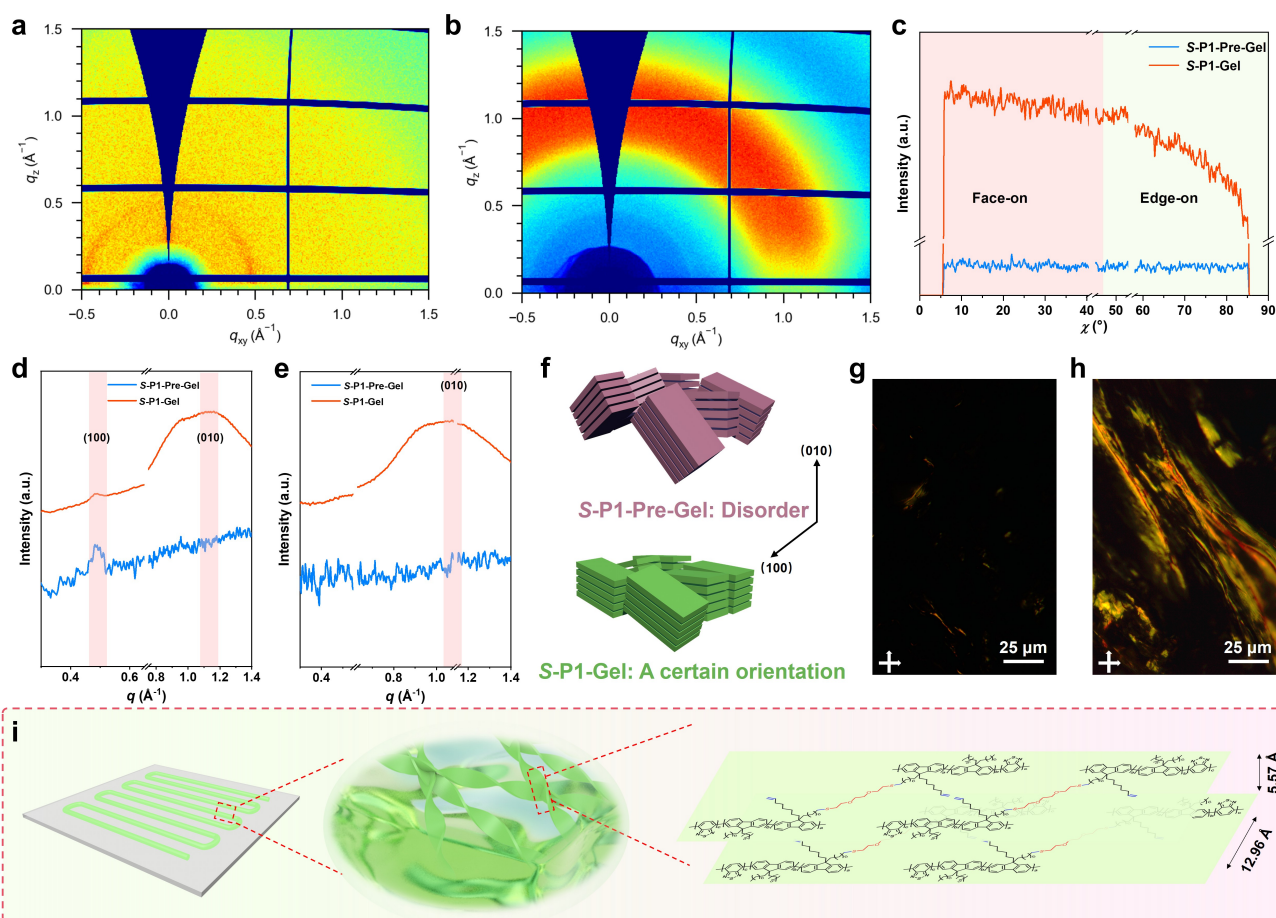


Fig. 4 Structural analysis of S-P1-Pre-Gel and S-P1-Gel. 2D-GIWAXS patterns of S-P1-Pre-Gel (a) and S-P1-Gel (b). (c) Normalized intensity distribution of the inner pattern as a function of the χ angle for different films in the q range of 1.00-1.04 $\text{\AA}^{-1}$. (d) 1D GIWAXS plots along the equatorial direction (in-plane). (e) 1D GIWAXS plots along the meridional direction (out-of-plane). (f) Schematic diagram of the chain orientation changes of the two gels. POM images of the S-P1-Pre-Gel (g) and S-P1-Gel (h). (i) Schematic diagram of supramolecular chirality orientation distribution and polymer chain stacking of S-P1-Gel.

The 1D plots obtained by integrating the 2D data exhibited similar (100) diffraction peak in the in-plane with the d spacing of 12.96 $\text{\AA}$ (**Fig. 4d**). In the out-of-plane direction, only **S-P1-Gel** showed a distinct diffraction peak with the d spacing of 5.57 $\text{\AA}$, corresponding to the π - π stacking between polymer chains

(Fig. 4e). Fig. 4f displayed differences in ordered orientation structures for the two gels, which may be attributed to the main reason for the chiral amplification. POM images further demonstrated the differences in internal structure between the two gels (Figs. 4g and h). Unlike the almost dark image of **S-P1-Pre-Gel**, **S-P1-Gel** exhibited distinct bright stripes, revealing the oriented structure and partial crystalline characteristics. Based on the above analysis, the schematic diagram summarized the structure of **S-P1-Gel** from the macroscopic to the microscopic levels, mainly including a distance of 12.96 Å between alkyl side chains and a distance of 5.57 Å between the main chains π - π stacking (Fig. 4i).

Taken together, the above results revealed that EITE process which involved chain orientation rearrangement, partial crystallization, and abundant non-covalent intermolecular forces, synergistically facilitated chiral amplification while strengthening the mechanical properties of the gels.

Universality study of the CMCDN and EITE methods for full-color CPL-active gels

To verify the universality of this strategy, we further synthesized other two similar polyfluorene derivatives by Yamamoto coupling reaction. The random polymer, PF8-*r*-F-Octene (abbreviated as PFO, noted as P2) and PF8-*r*-F-Octene-*r*-DTBT (abbreviated as PFO-DTBT, noted as P3) were synthesized by copolymerization of the corresponding achiral monomers (Supplementary Fig. 13), demonstrated by NMR and GPC measurements (Supplementary Figs. 14 and 15). The molecular weight (M_n) of P2 and P3 was 25,900 g mol⁻¹ and 30,400 g mol⁻¹ with the corresponding molecular weight distribution ($\mathcal{D}$) of 2.21 and 1.80, respectively. The ESP distribution of simplified P2 and P3 showed similar results with that of P1, demonstrating the possibility of forming a double-network structure with PMMA (Supplementary Fig. 16). As shown in Supplementary Fig. 17, both polymers can form precursor gels with CMCDN (noted as **S/R-P2-Pre-Gel** and **S/R-P3-Pre-Gel**, respectively) via thiol-ene micro-crosslinking reactions and following chiral assembly. Then the **S/R-P2-Gel** and **S/R-P3-Gel** can be prepared by the similar CMCDN and EITE methods (Fig. 5a). The FL spectra of the three polymer gels with S-limonene was given in Fig. 5b, displaying three fluorescent colors: green (P1), blue (P2), and red (P3), respectively. The characteristic emission peak at 442 nm and 467 nm of **S-P2-Gel** confirmed the formation of the β -phase structure⁵⁰. Notably, although the maximum emission peaks of the other two polymers showed a significant redshift (524 nm for P1 and 636 nm for P3), the characteristic emission peak of the fluorene unit remained intact, demonstrating their similar chain structure of fluorene units. CPL spectra and corresponding g_{lum} value curves indicated the formation of three pairs of chiral gels with opposite chirality via S/R-limonene induction

(Fig. 5c and Supplementary Fig. 18). The g_{lum} value of **S-P2-Gel** and **S-P3-Gel** reached up to 5.4×10^{-3} ($\lambda_{max} = 470$ nm) and 5.9×10^{-3} ($\lambda_{max} = 666$ nm), respectively. Another important parameter, quantum yield, was as follows: 26.9% for **S-P1-Gel**, 20.2% for **S-P2-Gel**, and 22.3% for **S-P3-Gel** (Supplementary Fig. 19).

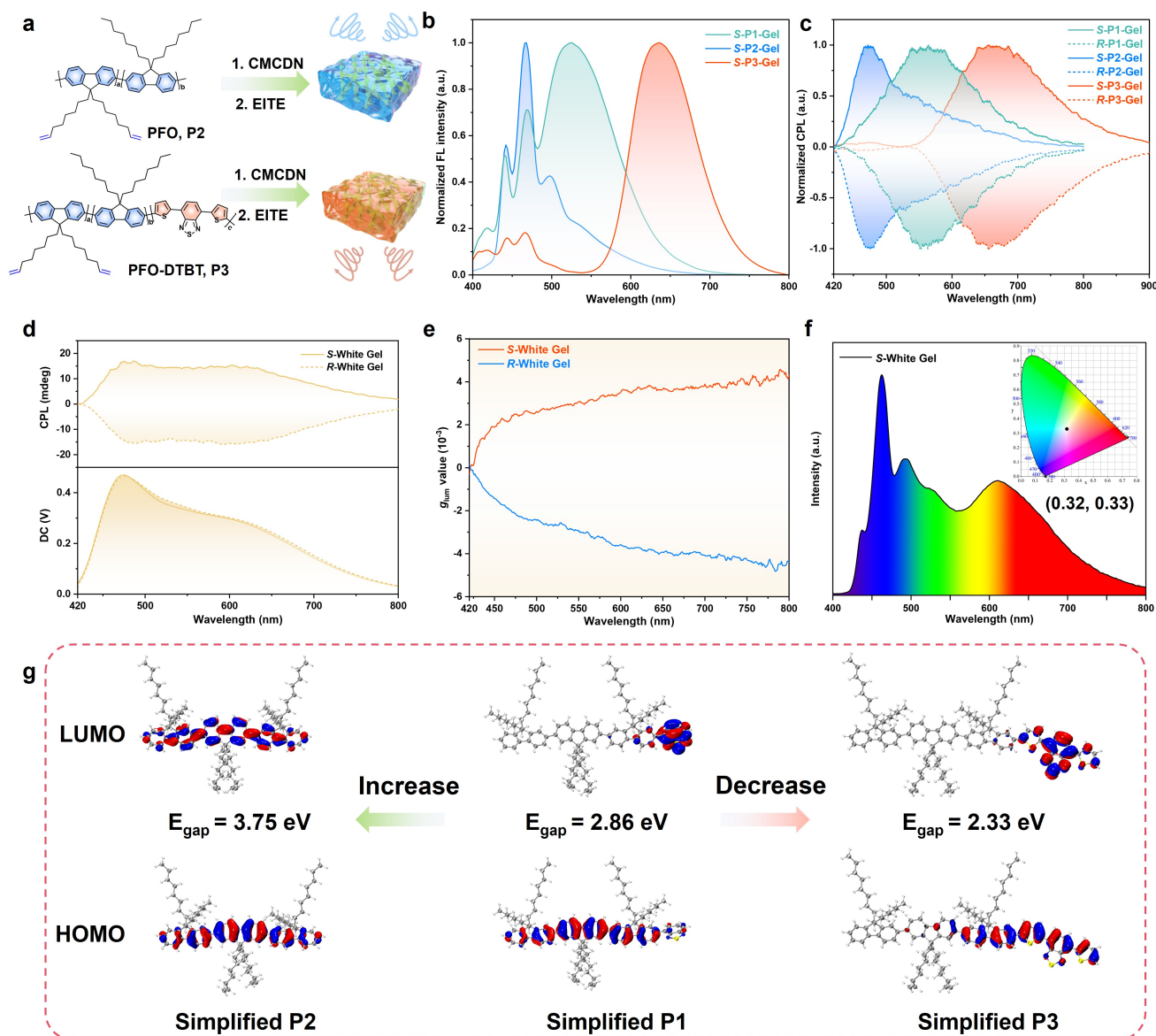


Fig. 5 Universality study of CMCDN and EITE methods for the preparation of full-color CPL-active gels. (a) Schematic illustration for the polymer chemical structures and corresponding CPL-active gels. (b) Normalized FL spectra of the P1, P2 and P3 gels prepared by S-limonene. (c) Normalized CPL spectra of the P1, P2 and P3 gels. (d) CPL spectra of S/R-white gels composed of P1, P2 and P3 in a certain proportion. (e) g_{lum} value curves of S/R-white gels. (f) FL spectra of the S-white gel. The inset is the CIE chromaticity coordinate. (g) 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 functional theory (DFT) calculations.

By precisely controlling the mass ratio of the three polymers (P1:P2:P3 = 1:3:0.5), a pair of white

fluorescent gels with opposite CPL was prepared (**Fig. 5d**). The CPL spectra and DC curve exhibited the characteristics of multi-wavelength emission. The g_{lum} value curves of S/R-white gels indicated a mirror-image chiral structure, and the g_{lum} value gradually increased with increasing wavelength (**Fig. 5e**). The FL spectra result was consistent with the CPL and DC curve results, showing the characteristics of multi-wavelength emission (**Fig. 5f**). The Commission Internationale de L'Eclairage (CIE) chromaticity coordinate of S-white gel was (0.32, 0.33), which was very close to the ideal white light coordinates (the inset in **Fig. 5f**). Furthermore, to explore the differences in the FL properties of the three polymers, density functional theory (DFT) calculations were conducted. As shown in **Fig. 5g** and **Supplementary Fig. 20**, for P1 and P2, the electron densities of both highest occupied molecular orbital (HOMO) were mainly distributed over the fluorene units. But the electron densities of the lowest unoccupied molecular orbital (LUMO) were clearly different. The electron densities of P1 were mainly delocalized on the BT units, exhibiting the intramolecular charge transfer (ICT) character, leading to a significant change of fluorescence maximum emission. Therefore, the HOMO energy level of P1 and P2 were similar but their LUMO energy level differed significantly. The E_{gap} of P1 and P2 was 2.86 eV and 3.75 eV, respectively. Unlike the previous two polymers, the electron densities of HOMO and LUMO of P3 were mainly concentrated on the DTBT units, resulting in a larger wavelength shift and a smaller E_{gap} value (2.33 eV).

Rational regulation through secondary crosslinking and 3D printing application

To meet the needs of complex practical applications, the mechanical and chiroptical properties of flexible materials require more precise control. The tetrathiol crosslinker, pentaerythritol tetra(3-mercaptopropionate) (PETMP), was used to regulate the gel structure by secondary crosslinking reaction with the residual double bonds in the polymer side chains (**Fig. 6a**). Before secondary crosslinking, all three robust polymer gels (**S-P1-Gel**, **S-P2-Gel**, and **S-P3-Gel**) exhibited excellent tensile properties, exceeding twice their original length (**Fig. 6b** and **Supplementary Fig. 21**). Stress-strain curves further proved the experimental results (**Fig. 6c**). Then after a highly efficient click reaction, the mechanical properties of the gels were significantly altered. As displayed in **Fig. 6d** and **Supplementary Table 1**, after only 20 seconds of crosslinking reaction, the tensile strain of **S-P1-Gel** decreased from 317.89% to 31.18%. Meanwhile, the Young's modulus increased from 0.78 MPa to 5.43 MPa. With extended crosslinking reaction time, the tensile strain of the gel decreased while its Young's modulus increased synchronously. Besides mechanical properties, the g_{lum} value was one of the most important parameters of flexible

1 chiroptical materials. CPL spectra of **S-P1-Gel** with different crosslinking time revealed that after 20
 2 seconds of crosslinking reaction, the CPL spectra remained essentially unchanged (**Fig. 6e**), but the signal
 3 gradually decreased as time further continued (**Supplementary Fig. 22**).

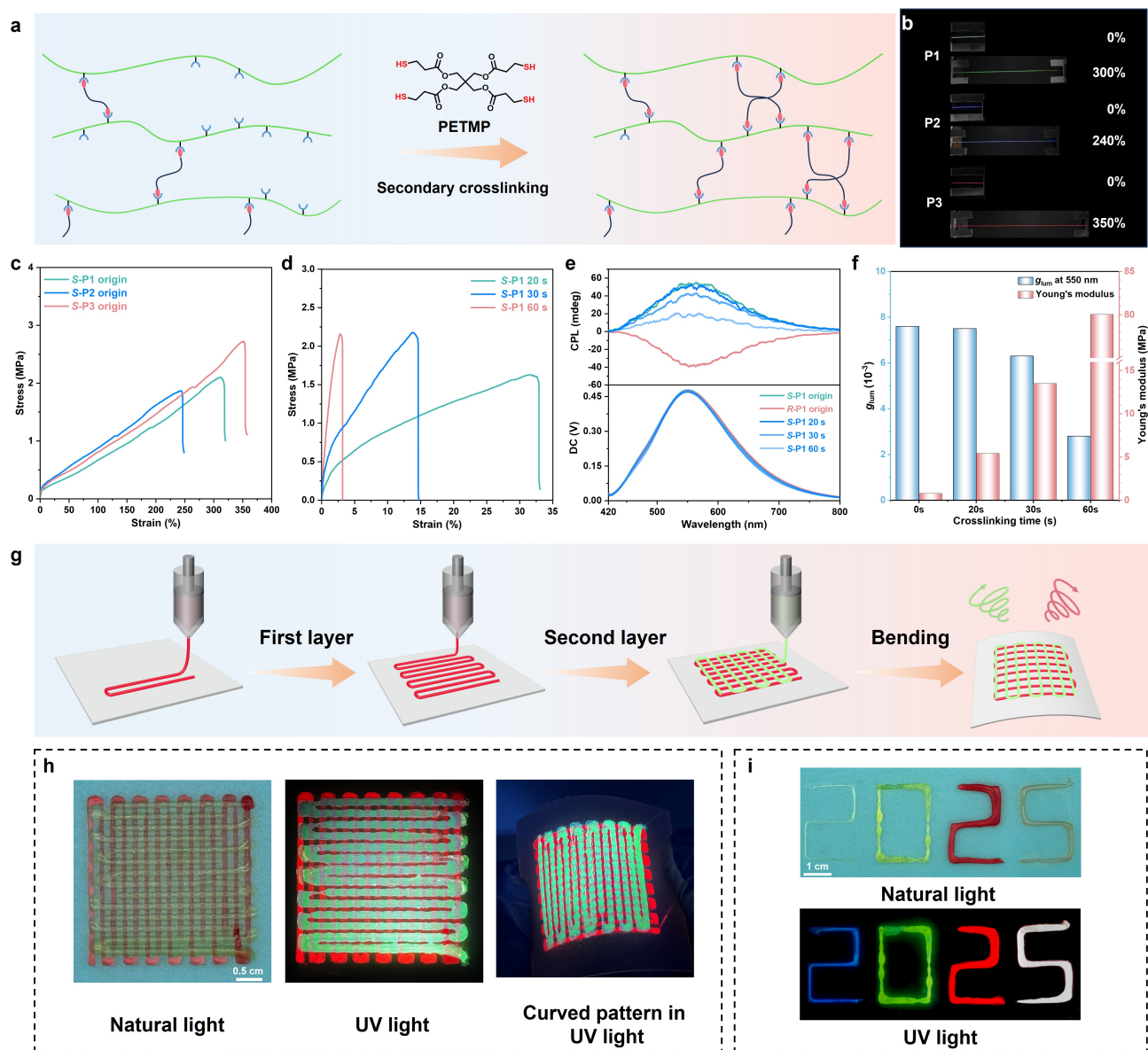


Fig. 6 Rational regulation of mechanical and chiroptical properties and 3D printing. (a) Schematic illustration for the secondary crosslinking process via tetrathiol crosslinker. (b) Digital photos of macroscopic stretching of S-P1-Gel, S-P2-Gel, and S-P3-Gel under 365 nm UV light. (c) Stress-strain curves of the original S-P1-Gel, S-P2-Gel, and S-P3-Gel without secondary crosslinking (noted as S-P1/2/3 origin for clarity). (d) Stress-strain curves of S-P1-Gel with different crosslinking time (noted as S-P1 seconds for clarity). (e) CPL spectra of S-P1-Gel with different crosslinking time. (f) g_{lum} value at 550 nm and Young's modulus of S-P1-Gel with different crosslinking time. (g) Schematic diagram explaining the process of 3D printing multi-layer materials using DIW and object bending diagram. (h) The digital photos of 3D-printed double-layer gel model under natural light and UV light as well as curved pattern in UV light. (i) The digital photos of full-color 3D printed models containing blue, green, red, and white under natural and UV light.

Fig. 6f summarized the variation of g_{lum} value and Young's modulus of **S-P1-Gel** with different

crosslinking time, showing that they have opposite trends. The results indicated excessive crosslinking can disrupt the chiral structure of the gel. The **S-P2-Gel** and **S-P3-Gel** exhibited similar trend of variation in mechanical and chiroptical properties, suggesting the universality of the secondary crosslinking strategy (**Supplementary Figs. 23-25** and **Supplementary Table 1**). Furthermore, we extended the precursor gel to an actual direct ink writing (DIW) 3D printer to scale up and automate the extrusion experiment. Unlike other 3D printing CPL-active materials, without the addition of any auxiliary resin, these polymer gel materials (**S-Pn-Pre-Gel** ($n = 1, 2$ and 3)) can be directly used in DIW 3D printing to form self-supporting objects (**Fig. 6g** and **Supplementary Fig. 26**). As shown in **Fig. 6h**, the double-layered structure was fabricated via DIW 3D printing with **S-P1-Pre-Gel** and **S-P3-Pre-Gel** employed alternately as printing inks, emitting bright green and red fluorescence under UV light. It was worth noting that the printed structure can be easily bent. In addition, four full-color digital patterns of “2025” were successfully printed, demonstrating the great potential of the gel materials for automated fabricating full-color flexible display devices (**Fig. 6i**). Moreover, thanks to the simplicity of this printing method, the 3D-printed objects showed almost identical CPL performance, laying a solid foundation for the large-scale and automated construction of flexible CPL materials (**Supplementary Fig. 27**).

Discussion

In conclusion, we developed a versatile chemical-physical synergistic strategy including chemical CMCDN and physical EITE methods to fabricate stretchable full-color CPL gels with tunable mechanical stiffness and CPL signals. Side-chain vinyl-functionalized polyfluorene derivative was successfully designed and synthesized. Partial thiol-ene micro-crosslinking generated polymer networks with reserved double bonds for post-modulation. Mixed with PMMA and chiral limonene, the double-network precursor gel showed shear-thinning rheology suitable for extrusion. Furthermore, extrusion induced shear-driven chain orientation and partial crystallization, alongside multiple non-covalent interactions (including van der Waals forces, C-H/O=C interaction, and π - π stacking). These synergistic effects substantially boosted the g_{lum} (7.8×10^{-3} at 551 nm of **S-P1-Gel**) and mechanical strength. Full-color CPL gels were realized via backbone bandgap engineering, proving the generality of this strategy. Finally, without extra commercial 3D printing materials, the precursor gels acted as printable DIW ink to construct self-supporting, bendable full-color 3D architectures with preserved chiroptical performance. This work overcomes the drawbacks of CPL materials, focusing on poor processability, limited stretchability and single-color emission. The stiffness-

adjustable full-color CPL gels are promising for flexible 3D displays, wearable anti-counterfeiting labels and chiral sensing, and guide large-scale and automated preparation of soft chiroptical devices.

Online Methods

Materials. 2,2'-(Ethane-1,2-diylbis(oxy))bis(ethane-1-thiol) (DODT) (95.0%, Aladdin, Shanghai, China), Pentaerythritol tetra(3-mercaptopropionate) (PETMP) (95.0%, Aladdin, Shanghai, China), *R*-limonene (>95%, $[\alpha]^{24}_{589} = +99.62^\circ$, TCI Shanghai Development Co., Ltd., Shanghai, China), *S*-limonene (>95%, $[\alpha]^{24}_{589} = -97.72^\circ$, TCI Shanghai Development Co., Ltd., Shanghai, China), 2,7-dibromo-9,9-di-*n*-octylfluorene (98.0%, TCI Shanghai Development Co., Ltd., Shanghai, China), bis(1,5-cyclooctadiene)nickel (0) (97.0%, Aladdin, Shanghai, China), 4,7-dibromo-2,1,3-benzothiadiazole (98.0%, TCI Shanghai Development Co., Ltd., Shanghai, China), 4,7-bis(5-bromo-2-thienyl)-2,1,3-benzothiadiazole (95.0%, Aladdin, Shanghai, China), 8-bromo-1-octene (98.0%, Macklin, Shanghai, China), 2,2'-Bipyridine (98.0%, Aladdin, Shanghai, China), 2,2-dimethoxy-2-phenylacetophenone (95.0%, Aladdin, Shanghai, China) and poly(methyl methacrylate) ($M_w = 300$ kDa, 98.0%, Aladdin, Shanghai, China) were used without further purification. All the other chemicals were obtained from Jiangsu Chemical Reagents (Jiangsu, China).

Preparation of polymer solutions with micro-crosslinked network (MCN)

In a typical experiment, thiol-ene click chemistry was utilized to construct polymer micro-crosslinked networks (MCN). First, 10 mg of PFO-BT polymer was placed into a 4 mL glass vial. Next, 2,2'-(ethane-1,2-diylbis(oxy))bis(ethane-1-thiol) (DODT) and the photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA) were separately dissolved in toluene to prepare DODT/toluene solution and DMPA/toluene solution, both at a concentration of $10 \text{ mg} \cdot \text{mL}^{-1}$. Afterwards, 71 μL of DODT/toluene stock solution, 39 μL of DMPA/toluene stock solution, and 390 μL of pure toluene were added sequentially to the vial containing P1. The mixture was stirred at 40°C for 30 min until P1 was fully dissolved and the Tyndall effect disappeared from the transparent solution. The total volume of the resulting solution was 500 μL , corresponding to a P1 concentration of $20 \text{ mg} \cdot \text{mL}^{-1}$ in toluene. Finally, the stirred mixture was placed 5 cm away from a 405 nm curing lamp (50 W) and irradiated for 12 h. After photocuring, the P1 MCN solution was obtained. The experimental procedures for the other two polymers (P2 and P3) are the same as above.

Preparation of S/R-P1-Pre-Gel with chiral micro-crosslinked double-network (CMCDN) structure

In a typical experiment, 200 μL of *S*-limonene and 100 mg of PMMA powder were first introduced into 500

1 μL of P1 MCN solution. The resulting mixture was stirred and heated at 65 °C for 10 h to completely
2 dissolve PMMA, yielding a viscous solution. Afterwards, the viscous solution was transferred into a 1 mL
3 syringe, followed by freezing at -20 °C for 36 h to afford precursor gel (S-P1-Pre-Gel). *R*-P1-Gel was
4 fabricated via an identical protocol, with the chiral additive replaced by *R*-limonene only.

5 **Preparation of S/R-P1-Gel via extrusion-induced topological evolution (EITE)**

6 The original needle of the syringe was then substituted with an extrusion needle possessing a diameter of
7 400 μm with a rate of 600 $\mu\text{L min}^{-1}$ to accomplish the formation of a robust gel (S-P1-Gel) by EITE. *R*-P1-
8 Gel was fabricated via an identical protocol, with the chiral additive replaced by *R*-limonene only. The
9 experimental procedures for the other two polymers (P2 and P3) are the same as above.

10 **Secondary crosslinking of the robust CPL-active gels**

11 An extruded gel strip with a length of approximately 3 cm was placed into a glass Petri dish with a diameter
12 of 60 mm, followed by the addition of 10 mL crosslinking solution to fully submerge the strip. The Petri dish
13 was positioned 5 cm away from a 405 nm curing lamp inside a light-shielded reaction chamber for
14 photoirradiation. The crosslinking solution contained PETMP at a concentration of 5 mL mL⁻¹ and DMPA
15 at 2 mg mL⁻¹.

16 **3D Printing test**

17 The DIW 3D printing was performed using a pneumatic-extrusion system (EAZAO, Hangzhou Regenovo
18 Biotechnology Co. Ltd., China). For this work, the desired model was sliced using the open-source
19 software Cura. Typically, the printing path was configured in a two-layer structure utilizing a 90° woodpile
20 strategy, wherein the second layer was rotated 90° relative to the first layer to form the lattice architecture.
21 To achieve multi-material fabrication, the printing process for the first layer was temporarily paused upon
22 completion. The material was then switched by replacing the syringe containing the different precursor gel.
23 The printing was resumed after the swap. The ink was loaded into 10 mL standard syringe barrel, with a
24 total volume of approximately 3-5 mL for each material and a tapered needle of 20 G.

25 **Density functional theory (DFT) calculations**

26 A series of DFT calculations were carried out by the Gaussian 16C package⁵². The models were optimized
27 at B3LYP/def2-SVP level, including the D3 version of Grimme's empirical dispersion correction with
28 Becke-Johnson damping. The single point energy of the optimal structures were obtained at B3LYP/def-
29 TZVP level, with the chloroform solvent using Solvation Model Based on Density (SMD)⁵³. Then the
30 HOMO-LUMO gap and surface electrostatic potential of the molecules were analyzed by Multiwfn and

shown with Visual Molecular Dynamics (VMD). The intermolecular weak interactions were analyzed by Multiwfn using the modified independent gradient model (mIGM) method⁵⁴.

¹H Nuclear Magnetic Resonance (NMR) measurement. ¹H NMR spectra was recorded on an NMR instrument (300 MHz, Bruker, Kalsruhe, Germany) using DMSO-*d*₆ or CDCl₃ as solvent, and tetramethylsilane (TMS) as the internal standard.

Gel-Permeation Chromatograph (GPC) measurement. The molecular weight (*M*_n) of the polymer and its molecular weight distribution (*D*) were determined by using a particle organogels-permeation Chromatograph (GPC, TOSOH HLC-8320). The flow rate of tetrahydrofuran (THF) mobile phase was 0.35 mL min⁻¹, and test temperature was 40 °C. Polymer molecular weights were calibrated using narrow molecular weight distribution PMMA standards. For the measurement, the sample was prepared at 2 mg mL⁻¹.

Fluorescence (FL) spectroscopy. FL spectra were measured on an Edinburgh FLS-980 Spectrophotometer at a scan rate of 500 nm min⁻¹, excitation slit of 5 nm and emission slit of 5 nm, wavelength range from 420 ~ 800 nm, and excitation wavelength of 360 nm. The quantum yields (QYs) of the polymer films were measured by Edinburgh FLS-980 Spectrophotometer using the integrating sphere method, with wavelength range from 340 ~ 800 nm, and excitation wavelength of 360 nm.

Circular Dichroism (CD) spectroscopy. CD spectra of the polymeric chiral films were measured using a JASCO J-1500 CD spectrometer (JASCO Hachioji, Tokyo, Japan) with scanning bandwidth of 2 nm, scanning speed of 500 nm min⁻¹, wavelength range of 200 ~ 600 nm, and the response time of 2 s.

Circularly Polarized Luminescence (CPL) spectroscopy. CPL/DC spectra were recorded at 25 °C using a JASCO CPL-300 spectrofluorescence polarimeter (Tokyo, Japan) with excitation slit width of 3,000 μm, emission slit width of 3,000 μm, scan rate of 500 nm min⁻¹, wavelength range from 420 ~ 900 nm and the response time of 1 s. The excitation wavelength is 360 nm. The *g*_{lum} is defined by formula: $g_{lum} = \Delta I/I = 2(I_L - I_R)/(I_L + I_R)$, where *I*_L and *I*_R are the intensities of the pure left and right-handed CPL, respectively. Experimentally, CPL was measured using a JASCO CPL-300 spectrometer, and the value of *g*_{lum} was obtained as $g_{lum} = [\text{ellipticity}/(32,980/\ln 10)]/\text{total fluorescence intensity at the CPL extremum}$.

Fourier Transform Infrared (FT-IR) spectroscopy. FT-IR spectra of the polymer before and after crosslinking were collected on a TENSOR 27 FT-IR spectrometer (Bruker, Germany).

Two-Dimensional Grazing Incidence Wide-Angle X-ray Scattering (2D GIWAXS). The grazing incidence GIWAXS were collected on the NFPS BL17B1 of Shanghai Synchrotron Radiation Facility

(SSRF). This beamline adopted PILATUS3 S_2M detector for GIWAXS. All samples of GIWAXS were radiate at 10 keV X-ray with an incident angle of 0.1°.

X-ray Photoelectron Spectroscopy (XPS). XPS measurements were performed on crosslinked polymer specimens with an ESCALAB 250XI instrument (Thermo Fisher Scientific) equipped with an Al K α X-ray source.

Polarized Optical Microscopy (POM). The cross-section morphology of the gels was measured by using polarized optical microscopy (CNOPTec BK-POL, China).

Rheological test. The rheological properties of the polymer gel were measured using a rotational rheometer (THERMO SCIENTIFIC, Germany). The measurement mode involved testing the storage modulus (G') and loss modulus (G'') at different frequencies under a constant strain of 1%. The test temperature was 25 °C, the sample volume was 0.4 mL, the rotor distance from the platform was 1.0 cm, and the test frequency was 1–10 Hz.

Tensile test. The tensile tests were carried on a universal testing machine (UTM) (Instron, USA) with a 50 N load cell. Tensile tests were performed at room temperature under a crosshead speed of 20.0 mm·min⁻¹. Tensile strength was calculated by dividing the maximum load (N) by the average original cross-sectional area (m²) in the gage length segment of the specimen.

Data availability

All other data generated in this study, including experimental and synthetic procedures, compound characterization, NMR, GPC, FT-IR, XPS, FL, POM, GIWAXS, CD, CPL, rheological test, tensile test and theoretical calculations, are available within the article and its Supplementary Information or from the corresponding authors. Source data are provided with this paper.

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Author contributions

G.Z., W.Z., Z.H., and Z.Z. conceived the idea for this project. G.Z., Z.L., and N.W. performed the experiments, and analyzed the data. G.Z. produced the artwork and wrote the draft. J.Z. contributed to the

theoretical calculations. R.X. Z.L. and N.W. performed the 3D printing experiments. All authors contributed to the manuscript.

Conflict of interest

The authors declare no conflict of interest.

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