

## Electronic Supporting Information

### **Circularly Polarized Luminescent Organogels based on Fluorescence Resonance Energy Transfer in an Achiral Polymer**

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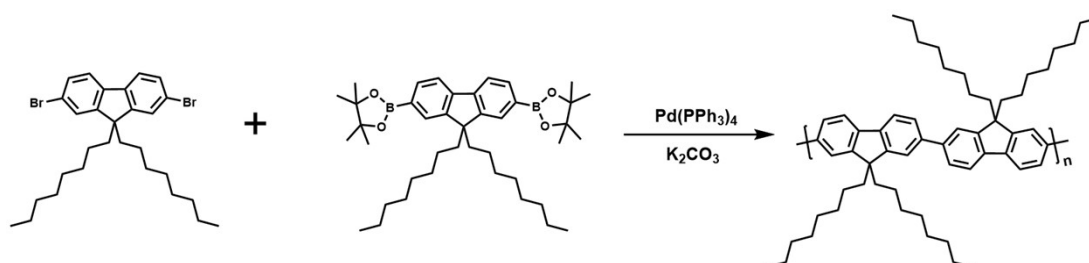
## MATERIALS AND METHODS

### Experimental Section

**Materials.** Tetrakis(triphenylphosphine) palladium (0) (97.0%, TCI, Tokyo, Japan), 2,7-dibromo-9,9-di-*n*-octylfluorene (98.0%, TCI Shanghai Development Co., Ltd., Shanghai, China), and 9,9-dioctylfluorene-2,7-diboronic acid (98.0%, J&K Scientific, Beijing, China) were used as received. Coumarin 6 and 3-amino coumarin (98.0%, J&K Scientific, Beijing, China), *R*-limonene (>95%,  $[\alpha]_{589}^{24} = +99.62^\circ$ , Shanghai Development Co., Ltd., Shanghai, China) and *S*-limonene (>95%,  $[\alpha]_{589}^{24} = -97.72^\circ$ , Shanghai Development Co., Ltd., Shanghai, China) were used without further purification. All the other chemicals were obtained from Shanghai Chemical Reagents (Shanghai, China). Poly(9,9-di-*n*-octylfluorene) (PF8) was synthesized according to the modified reported procedures.<sup>1</sup> All reagents and solvents were used as received without further purification.

**Synthesis of PF8.** In a typical experiment, 2,7-dibromo-9,9-dioctyl-9*H*-fluorene (171.0 mg, 0.311 mmol), 2,2'-(9,9-dioctyl-9*H*-fluorene-2,7-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (200.0 mg, 0.311 mmol), tetrakis(triphenylphosphine) palladium (10.2 mg, 0.00883 mmol), THF (4.5 mL) and 2.0 M potassium carbonate aqueous solution (3.0 mL) were mixed in Schlenk tube. The mixed solution was violently stirred at 80 °C for 72 h after three times of deoxygenation. Finally, crude product was poured into 500 mL MeOH/H<sub>2</sub>O (10:1, v/v), crude product cake was obtained by precipitation and filtration. Finally, the soil yellow polymer PF8 was obtained after extraction with

acetone for three days and drying with 30 °C, the yield is about 55%.  $M_n = 32\,300$  g/mol,  $D = 3.26$ .  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ ):  $\delta(\text{ppm})$  7.94-7.55 (m, 6H), 2.33-1.97 (s, 4H), 1.41-0.95 (s, 20H), 0.94-0.55 (s, 10H).



**Preparation of PF8 chiral organogels.** First, the preparation of  $10\text{ mg mL}^{-1}$  PF8 solution in limonene: 20 mg of polymer was added into a transparent sealed vial containing 2 mL of *R*-limonene solvent and heated with stirring at 80 °C for 4 h to bring the polymer to the molecular level of solubilization (no Tyndall effect by laser irradiation). After the temperature of the solution returned to room temperature, the solution was filtered through a  $0.45\ \mu\text{m}$  organic phase filter tip to remove large particles of impurities. Then 500  $\mu\text{L}$  of PF8 solution and 500  $\mu\text{L}$  of the *R*-limonene solution were added into the vial. The vial was completely sealed and assembled by freezing at -20 °C for 5 h. The polymer solution was found to be light green organogels. The vial was inverted at room temperature to demonstrate the formation of organogels. *S*-PF8 organogels were prepared in a similar way.

**Preparation of PF8@7.5%Cou6 chiral organogels.** In a typical experiment, we first prepared  $10\text{ mg mL}^{-1}$  PF8 solution in *R*-limonene solvent, and 2.44 mM coumarin 6 (Cou6) solution in *R*-limonene solvent, respectively. And then the as-prepared 500  $\mu\text{L}$  of PF8 limonene solution, 375  $\mu\text{L}$  of Cou6 limonene solution, 125  $\mu\text{L}$  of *R*-limonene

were mixed and co-assembled by freezing at -20 °C for 5 h. The polymer solution was found to be a green organogels. The vial was inverted at room temperature to demonstrate the formation of organogels. *S*-PF8@7.5%Cou6 organogels and *R*-PF8@7.5% 3-Cou were prepared in a similar way. Other organogels including different ratios of Cou6 were prepared in a similar manner as described above.

### **Characterization Methods**

**<sup>1</sup>H NMR measurement.** <sup>1</sup>H NMR spectra was recorded on an NMR instrument (300 MHz, Bruker, Kalsruhe, Germany) using CDCl<sub>3</sub> as solvent and tetramethylsilane (TMS) as the internal standard.

**GPC measurement.** The molecular weight ( $M_n$ ) of the polymer and its molecular weight distribution ( $\mathcal{D}$ ) were determined by using a particle organogels-permeation Chromatograph (GPC, TOSOH HLC-8320). The molecular weight detection range of the instrument is 500 ~  $1.9 \times 10^5$  g mol<sup>-1</sup>, the flow rate of tetrahydrofuran (THF) mobile phase is 0.35 mL min<sup>-1</sup>, and the test temperature is 40 °C. Polymer molecular weights were calibrated using narrow molecular weight distribution polystyrene (PS) standards. For the measurement, the sample was prepared at 2 mg mL<sup>-1</sup>.

**UV-vis measurement.** The UV-Vis absorption spectra of the polymer organogels and guest molecules solution were measured using a UV-Vis spectrometer (UV-2600, Shimadzu) with the slit width of 5 nm.

**CD spectra.** The CD spectra of the polymeric chiral organogels was measured using a circular dichroism spectrometer (JASCO J-815, JASCO Hachioji, Tokyo, Japan) with

scanning bandwidth of 2 nm, scanning speed of 200 nm min<sup>-1</sup>, wavelength range of 300 ~ 600 nm, and the response time of 2 s.

**CPL measurement.** CPL/FL spectra were recorded at 25 °C using a JASCO CPL-300 spectrofluorescence polarimeter (Tokyo, Japan) with excitation slit width of 3000 μm, emission slit width of 3000 μm, scan rate of 500 nm min<sup>-1</sup>, wavelength range from 400 ~ 700 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.<sup>2,3</sup> Experimentally, CPL was measured using a JASCO CPL-300 spectrometer, and the value of  $g_{lum}$  was obtained as  $g_{lum} = 2 \times [\text{ellipticity}/(32\ 980/\ln 10)]/\text{total fluorescence intensity at the CPL extremum}$ .<sup>4</sup>

**Fluorescence spectra test.** FL spectra was measured on an F-4600 FL Spectrophotometer at a scan rate of 1200 nm min<sup>-1</sup>, excitation slit of 5 nm and emission slit of 5 nm, wavelength range from 420 ~ 700 nm, and excitation wavelength of 360 nm. Energy transfer efficiency ( $\Phi_{ET}$ ) was calculated according to the formula:  $\Phi_{ET} = 1 - I_{DA}/I_D$ , where  $I_{DA}$  and  $I_D$  represent the fluorescence intensity of the donor in the presence and absence of the acceptor, respectively.<sup>5</sup>

**Fluorescence lifetime measurement.** Fluorescence decay spectra was recorded by using time-correlated single photon counting (TCSPC) at Edinburg FLS-980 fluorescence spectrometer. The fluorescence lifetime in this study was calculated by the following formula:

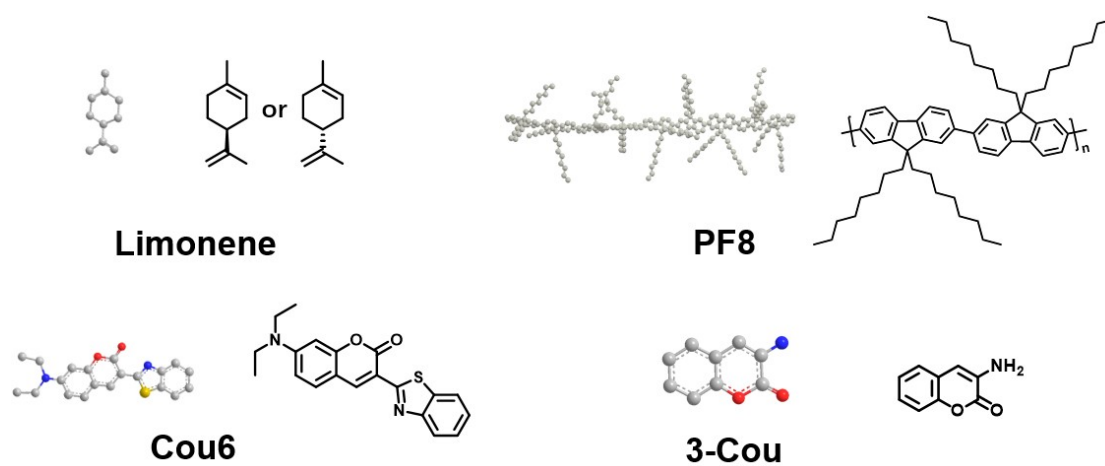
$$\tau = \tau_1 * Rel_1\% + \tau_2 * Rel_2\%$$

**AFM measurement.** AFM images were captured on a Multimode 8 microscope (Bruker Co. USA). Peak force quantitative nanomechanical mapping (QNM) in air scan mode with a ScanAsyst-air probe (nominal spring constants  $0.4 \text{ N m}^{-1}$ , a frequency of 70 kHz; Bruker) was adopted.

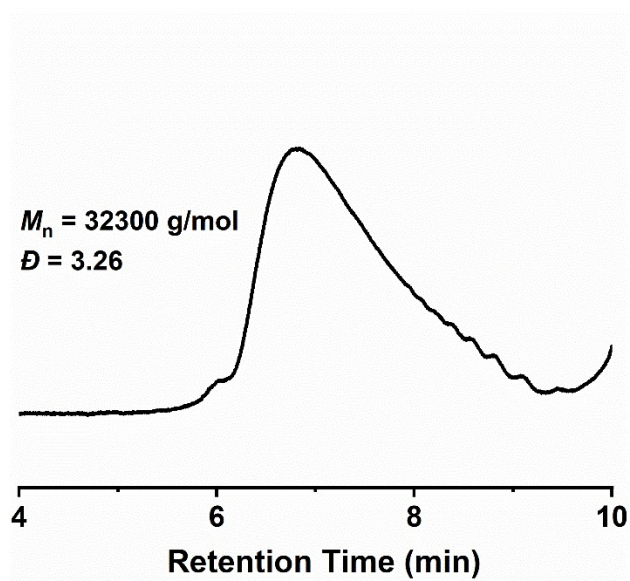
**HRTEM measurement.** HRTEM images were captured with a HITACHI HT7700 operated at an accelerating voltage of 120 kV.

**Rheology test.** The rheological tests were performed on an advanced rotational rheometer (Thermo Scientific, Germany). The dynamic frequency scan mode was performed at a strain of 0.1% and a frequency from 0.1 to 10 Hz. The static time scan mode was performed at a strain of 0.1%, a frequency of 1 Hz and a time of 60 s.

## SUPPORTING FIGURES



**Figure S1.** Structure information of the co-assembled components in this work.



**Figure S2.** GPC curve of PF8 polymer synthesized by Suzuki polycondensation reaction.

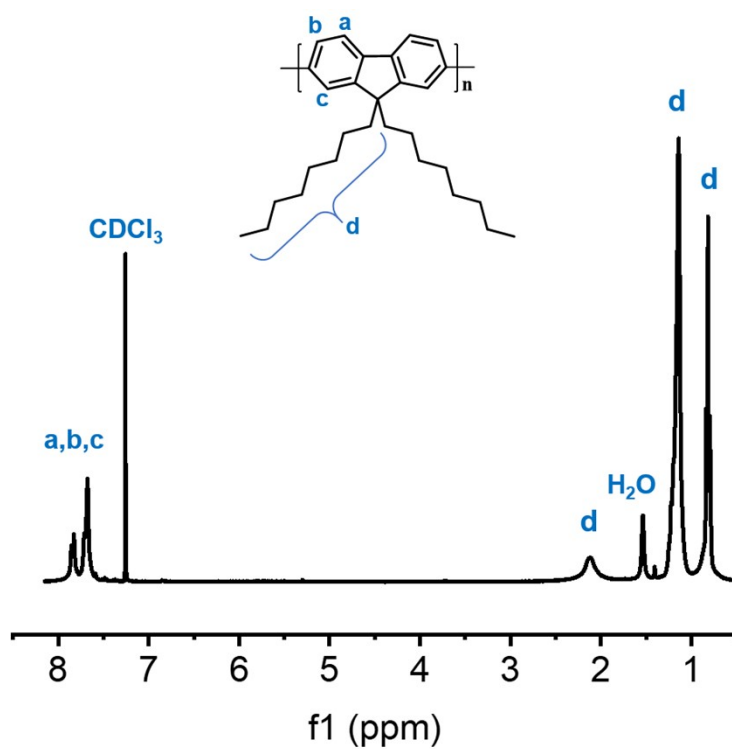


Figure S3. <sup>1</sup>H NMR data of PF8 polymer.

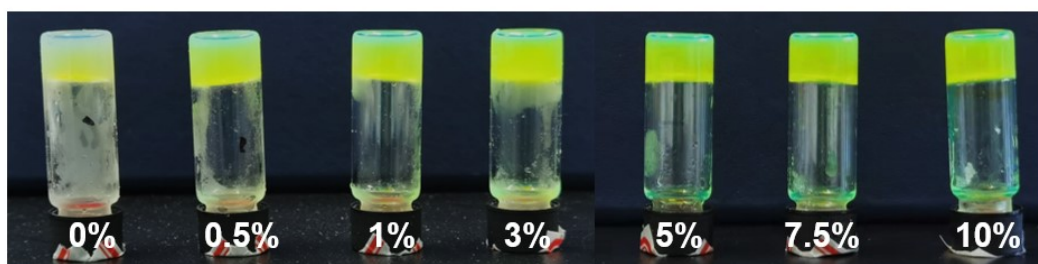
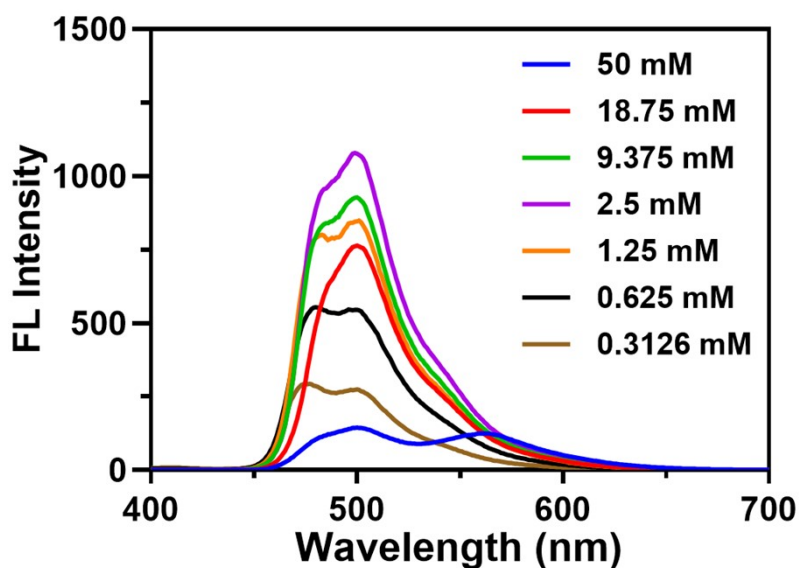


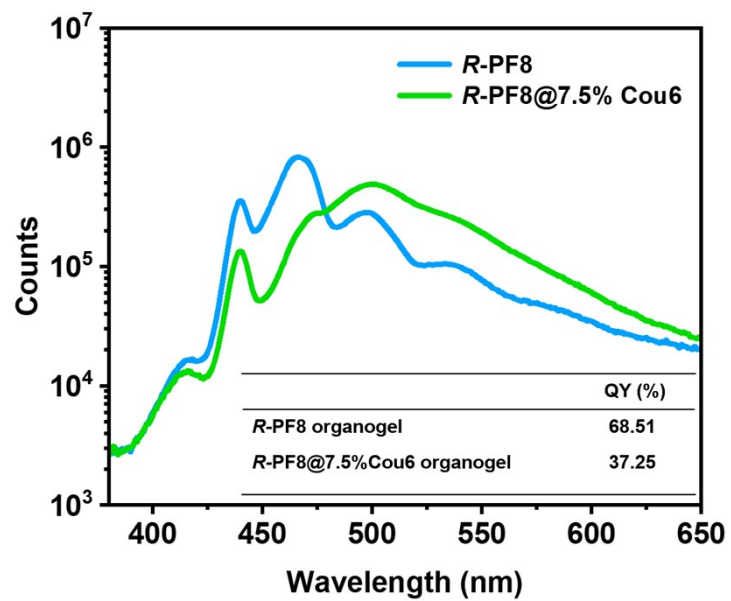
Figure S4. Optical images of the inverted tube experiment of typical *R*-PF8@Cou6 organogels with various Cou6 molar ratios under ambient light.



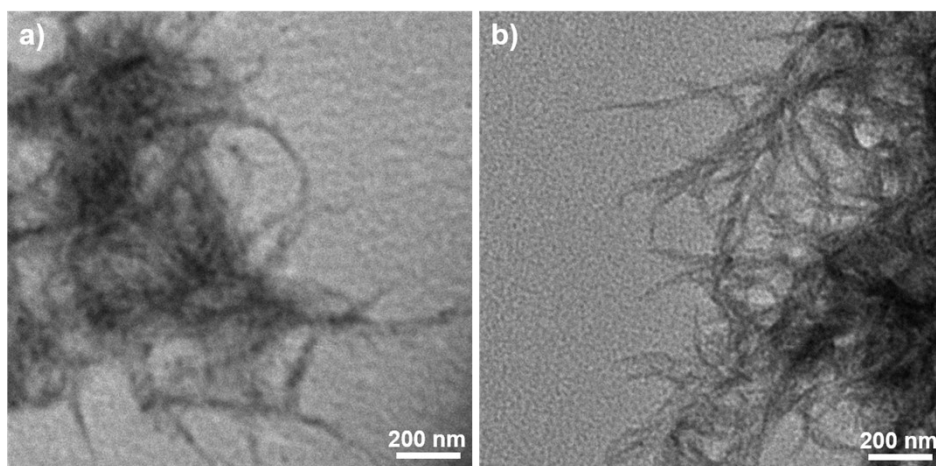


**Figure S5.** FL spectra of Cou6 in *R*-limonene solution with different concentrations at 20 °C.

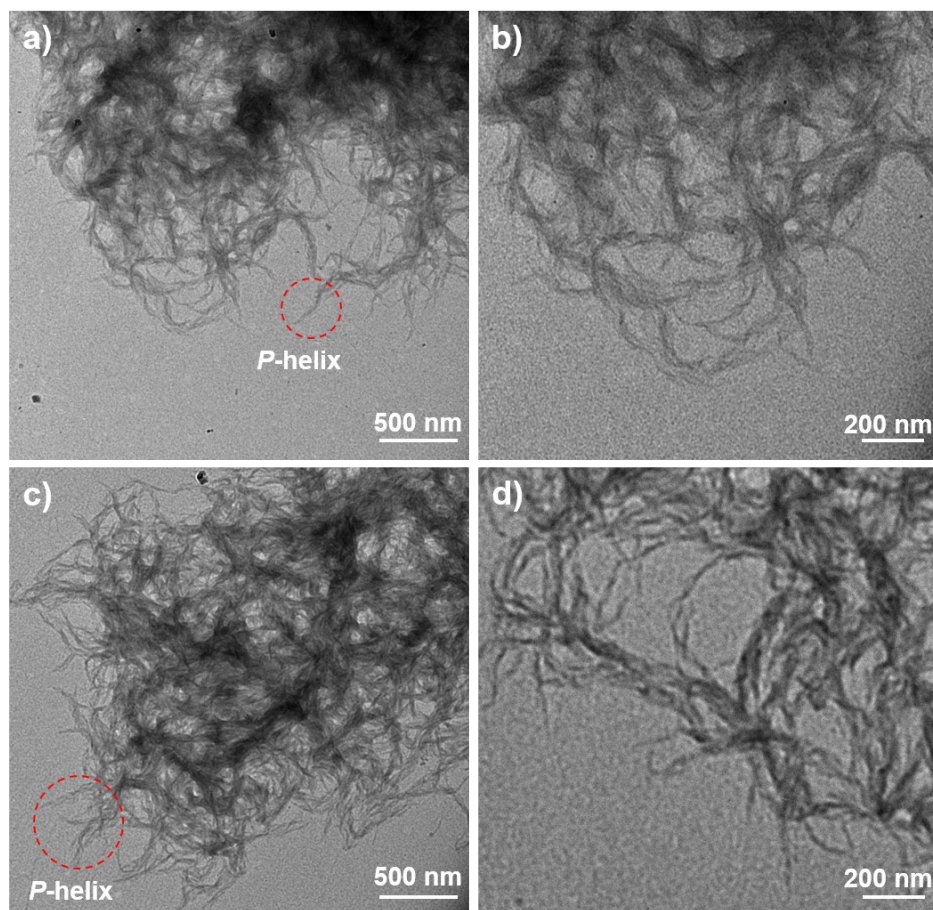
We have performed the fluorescence intensity measurement of Cou6 in *R*-limonene solution against different concentrations at 20 °C. As shown in **Figure S5**, in the concentration range of 0.3126 mM to 2.5 mM, the fluorescence intensity gradually increased with increasing concentration. But as the concentration further increased, the fluorescence intensity began to decrease. The phenomenon demonstrated the aggregation-caused quenching (ACQ) effect of Cou6 in limonene solution. Especially, when the concentration reached to 50 mM, very weak fluorescence intensity was measured, accompanied by the precipitation of a large number of Cou6 crystals. Moreover, the red-shift of the fluorescence peak occurred due to the intermolecular aggregation. It should be noted that the critical ACQ concentration of Cou6 in limonene solution and organogel system are very different. Because in the organogel system, the Cou6 molecules are easier to aggregate.



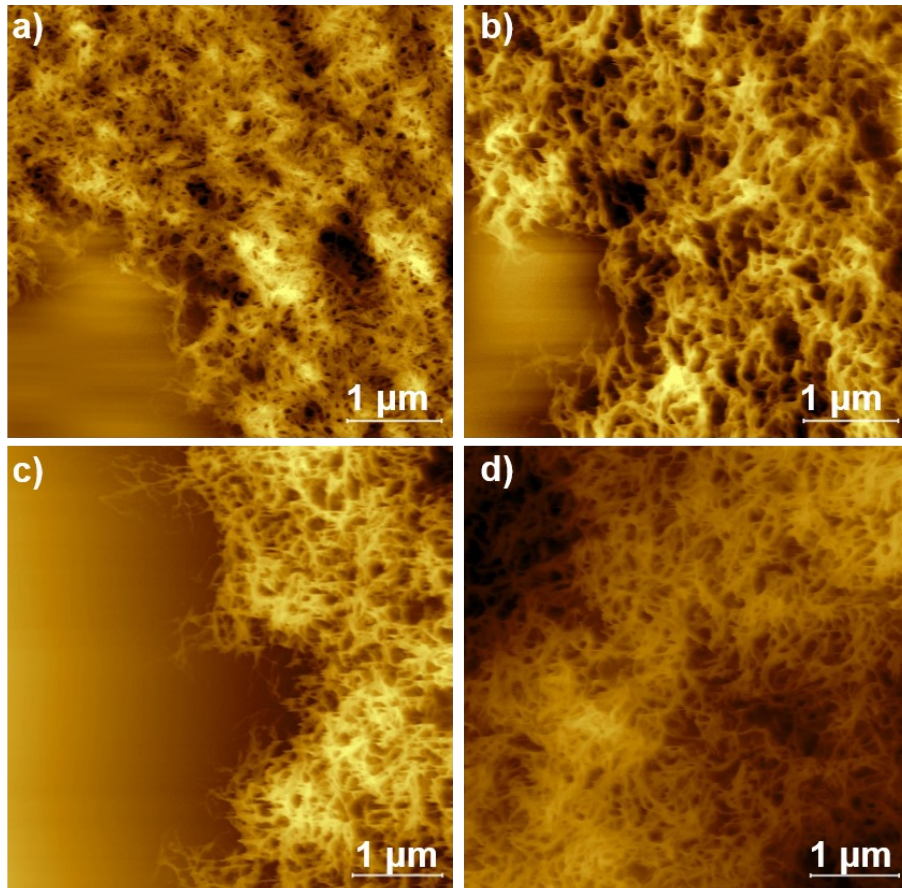
**Figure S6.** The absolute quantum yields of *R*-PF8 and *R*-PF8@7.5% Cou6 organogels.



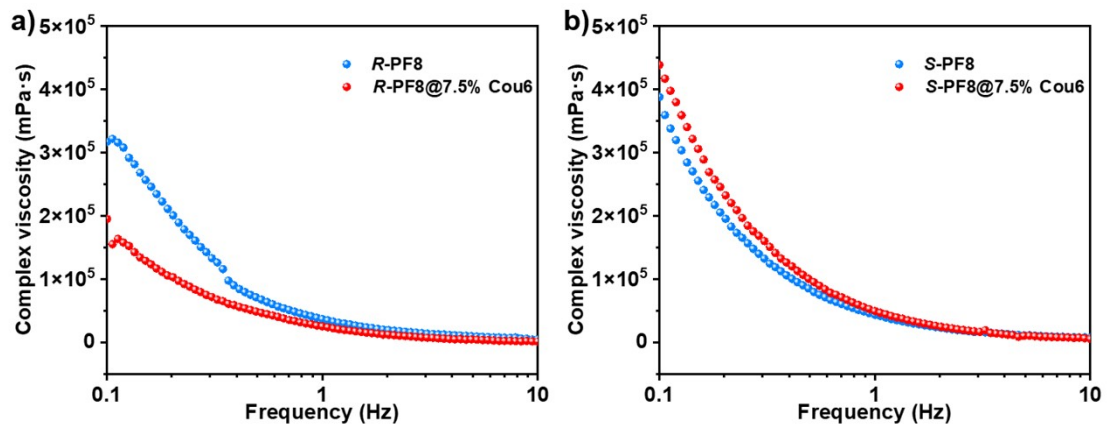
**Figure S7.** HRTEM images of *S*-PF8 and *S*-PF8@7.5% Cou6 organogels.



**Figure S8.** HRTEM images of a, b) *R*-PF8 and c, d) *R*-PF8@7.5%Cou6 organogels. The red circles in a) and c) show the change of screw pitch.



**Figure S9.** AFM images of a) *R*-PF8, b) *R*-PF8@7.5% Cou6, c) *S*-PF8, and d) *S*-PF8@7.5% Cou6 organogels.



**Figure S10.** Complex viscosity of *R/S*-PF8 and *R/S*-PF8@Cou6 organogels at a strain of 0.1% and at 25 °C.

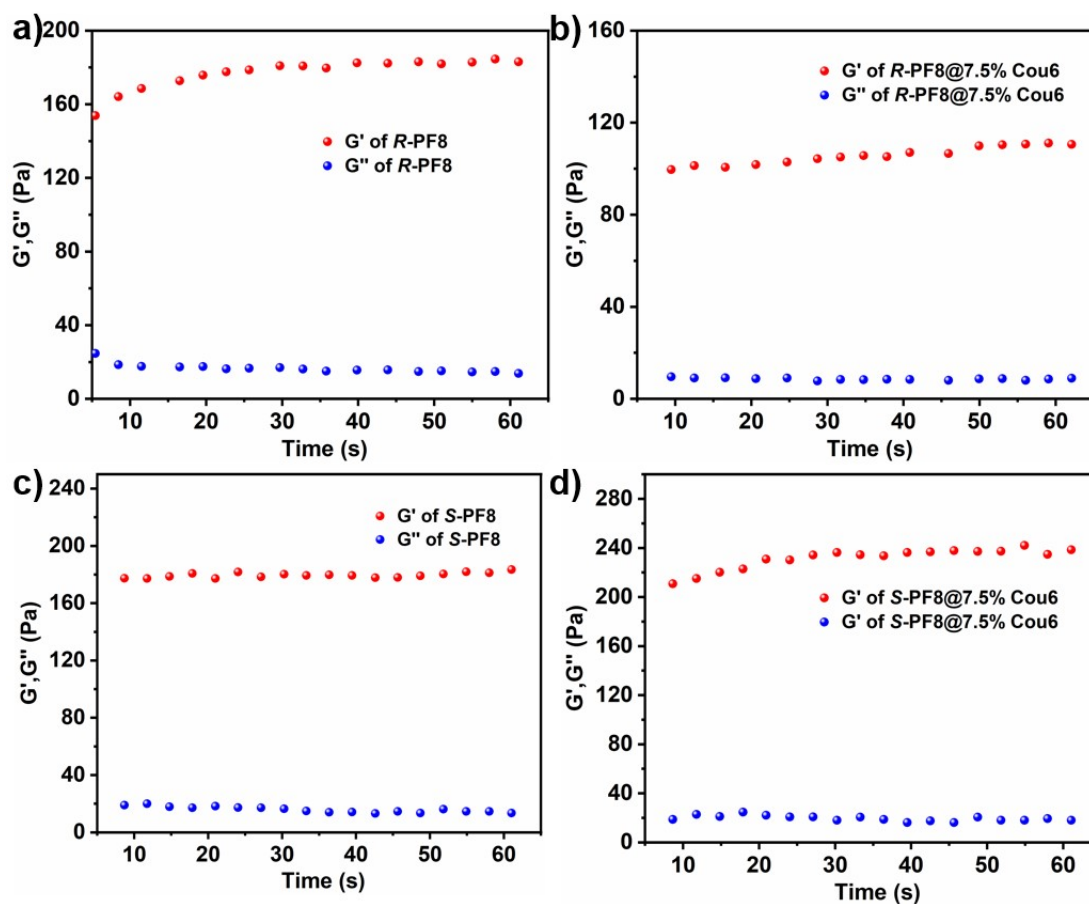


Figure S11. Static frequency sweep of organogels for 60 seconds at a strain of 0.1% and at 25 °C.

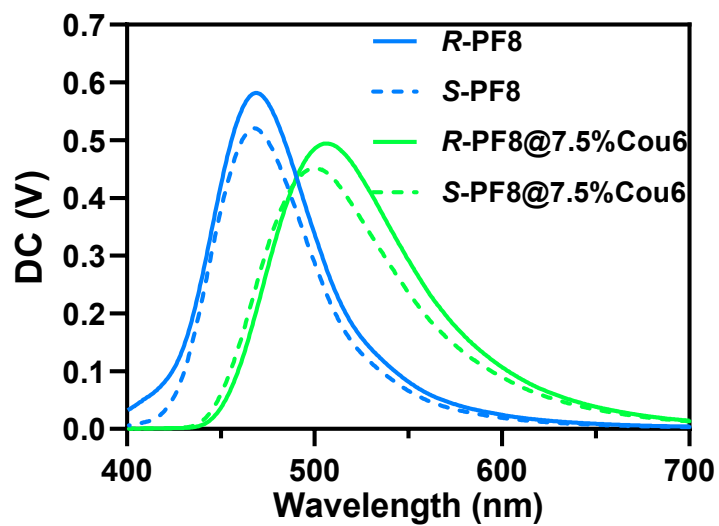
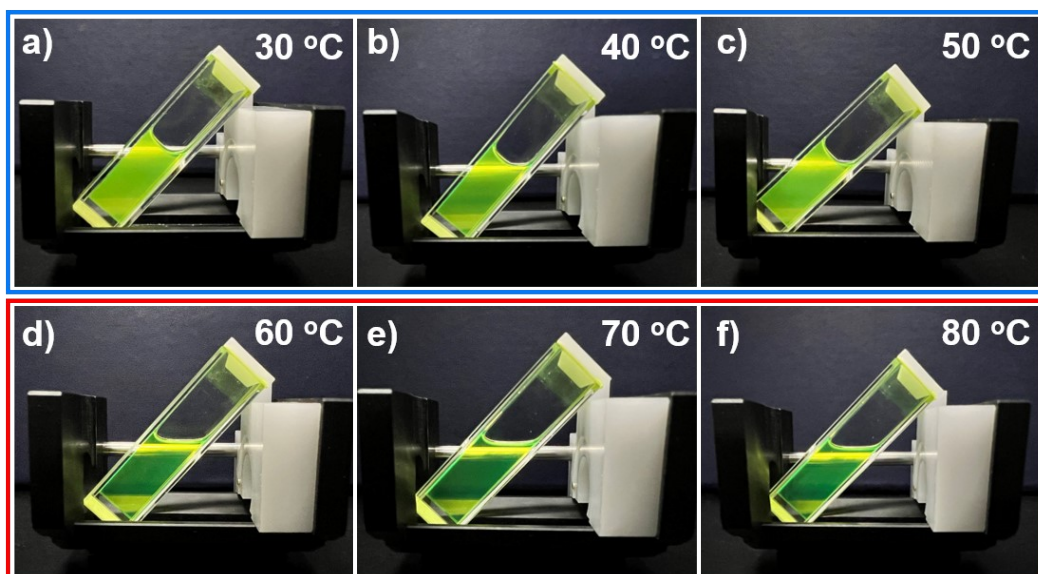
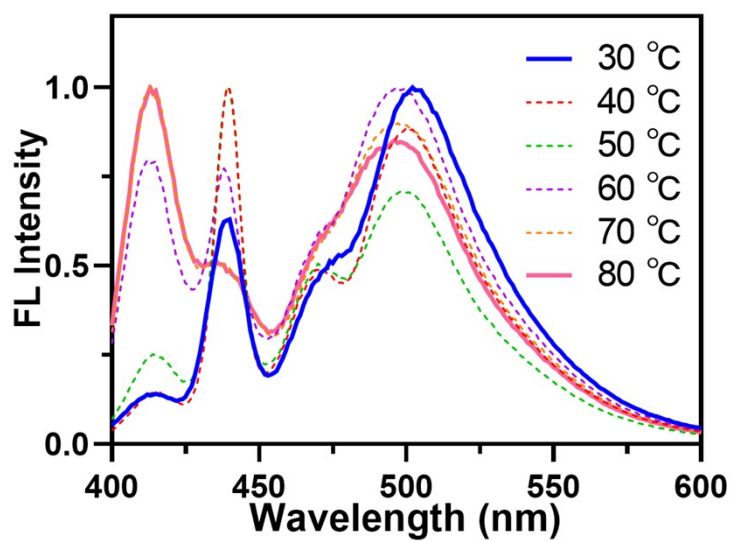


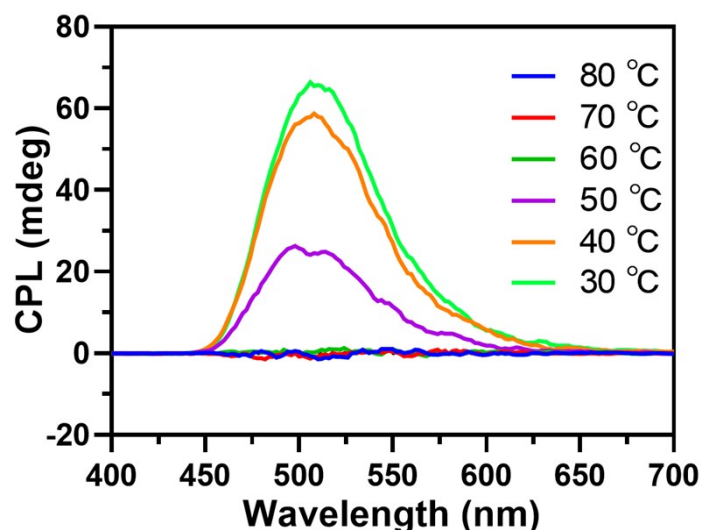
Figure S12. DC curve of *R/S*-PF8 and *R/S*-PF8@7.5% Cou6 organogels.



**Figure S13.** Optical images of the inclined tube experiment of typical *S*-PF8@Cou6 organogels under ambient light with different heat treatments for 10 minutes. The blue box represents the gel state. The red box represents the almost solution state.

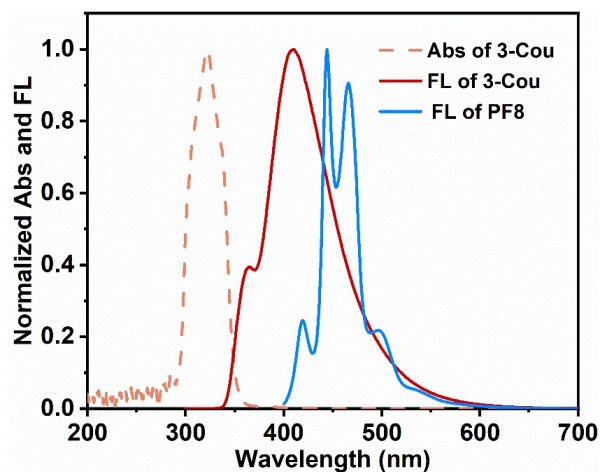


**Figure S14.** FL spectra of *S*-PF8@Cou6 organogels with different heat treatments for 10 minutes.

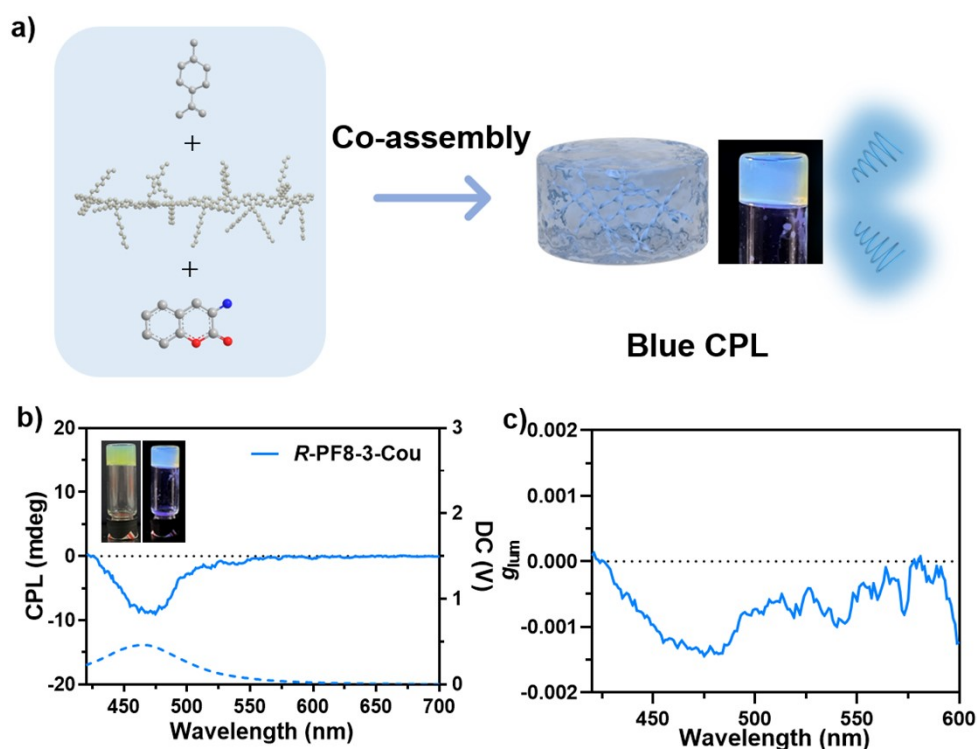


**Figure S15.** CPL spectra of S-PF8@Cou6 organogels with different heat treatments for 10 minutes.

As shown in **Figure S13**, the heat treatment experiment of the as-prepared S-PF8@Cou6 organogel was supplemented. The blue box represented the gel state. And the red box represented the almost solution state. The result indicated that the gel structure basically collapsed when the temperature  $> 50$  °C. A clear and transparent solution could be observed (**Figures S13d-f**). The fluorescence spectra of S-PF8@Cou6 organogel with different heat treatment for 10 minutes was measured. As shown in **Figure S14**, we found that the energy transfer efficiency of the gel gradually decreased with increasing temperature because the relative FL strength of PF8 gradually increased. When the temperature reached 80 °C, the emission changed. This was attributed to the phase state change of PF8 in limonene solution (from  $\beta$  phase to  $\alpha$  phase).<sup>1</sup> This result also indicated energy transfer process could occur in solution but with lower energy transfer efficiency. Because in the solution state, PF8 polymer and Cou6 molecules were molecularly dispersed in the solvent and the relative orientation was rapidly changing. The CPL performance also showed a gradually decreasing trend with temperature increase (**Figure S15**). When the gel structure collapsed ( $> 50$  °C), the CPL signals were almost silent.



**Figure S16.** Normalized UV-vis spectra and FL spectra of 3-Cou solution in limonene and FL spectra of PF8 organogels.



**Figure S17.** a) Schematic illustration of the co-assembly process of *R/S*-limonene, PF8 and 3-Cou; b) CPL spectra and c)  $g_{lum}$  curve of *R*-PF8@7.5% 3-Cou organogels. The inset shows the digital photos of *R*-PF8@7.5% 3-Cou organogels under ambient light and UV irradiation, respectively.

**Table S1.** The fitted parameter of fluorescence lifetime of different organogels at 444 nm.

Entry	$\tau_1$	$\tau_2$	$\tau$	$\chi^2$
PF8	0.44 (96.80%)	5.00 (3.20%)	0.59 ns	1.280
PF8@Cou6	0.20 (90.02%)	1.45 (9.98%)	0.32 ns	1.258

## References



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