

Supporting Information

Real-time Monitoring of Turbidity Changes of Solution Induced by Polymer Nanoparticle Using Fluorescent Probes

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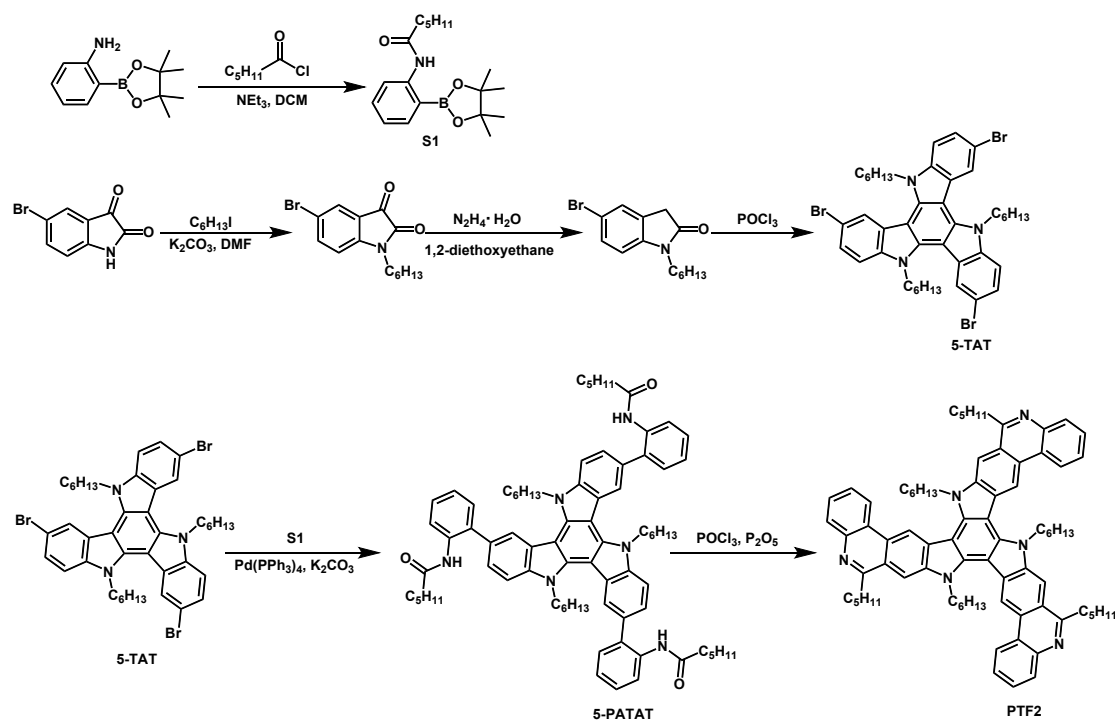
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1. Instruments

All Nuclear Magnetic Resonance (NMR) spectra were recorded using Bruker AVANCE III NMR 400M instrument. UV-vis absorption spectra were measured using a Shimadzu UV-2600 spectrophotometer. Fluorescence emission spectra were acquired using an Edinburgh FLS1000 spectrometer. Dynamic light scattering (DLS) experiments were performed on a Brookhaven BI-200SM light scattering instrument, and the molecular weight of the polymers was determined by gel permeation chromatography (GPC) using a Waters 1515-2414 system. Optical microscopy images were captured using a CNoptec-BK-POL microscope.

2. Synthesis of materials

2.1 Synthesis of PTF2



Scheme S1. Synthetic routes of **PTF2**

PTF2 was synthesized according to our previous study (*Adv. Mater.* **2022**, *34*, 2201337)^[1]. The specific procedures are outlined below:

S1: Weigh 2-amino phenylboronic acid ester (6 g, 27.3 mmol) and add it to a 500 mL round-bottom flask with 150 mL DCM . Seal the flask with a rubber stopper and place it in an ice-water bath at 0°C while stirring for 15 minutes. Slowly inject 5.7 mL of triethylamine into the

round-bottom flask using a syringe. The reaction is exothermic and produces white smoke. After the triethylamine is completely added, continue stirring at 0°C in the ice bath for an additional 15 minutes. Slowly inject 30 mL of DCM-diluted hexanoyl chloride (4.02 mL, 29.53 mmol) into the flask using a syringe. Maintain the reaction temperature at low temperature for 5 h.

After the reaction is complete, add 200 mL of deionized water to the flask. Extract the mixture with DCM (100 mL × 3), combine the organic phases, and dry over anhydrous sodium sulfate. Filter the solution and evaporate the organic solvent to obtain a yellow-brown oily liquid. Purify the product using a silica gel column chromatography (eluent: ethyl acetate/petroleum ether (1/10-1/5, v/v)). The final product obtained is an orange solid. ¹H NMR (400 MHz, Chloroform-d) δ 9.83 (s, 1H), 8.26 (d, J = 8.0 Hz, 1H), 7.76 (dd, J = 7.5, 1.7 Hz, 1H), 7.49 – 7.37 (m, 1H), 7.09 (td, J = 7.4, 1.1 Hz, 1H), 2.29 (t, J = 7.7 Hz, 2H), 1.71 (dd, J = 15.3, 7.8 Hz, 4H), 1.39 (s, 16H), 1.04 – 0.84 (m, 3H).

5-bromo-1-hexylindole-2,3-dione: 5-bromoindole-2,3-dione (10.0 g, 44.24 mmol), 1-iodohexane (11.25 g, 53.088 mmol), potassium carbonate (18.3 g, 132.72 mmol) and DMF (50 mL) were stirred at 70°C under nitrogen atmosphere overnight. Subsequently, after cooling to room temperature, the resulting mixture was poured into water and extracted with DCM for three times. The combined organic phases were dried over anhydrous sodium sulfate (Na₂SO₄), filtered, and evaporated to dryness. The crude product was purified on a silica gel column (eluent: dichloromethane and petroleum ether (1/5, v/v)) to give 5-bromo-1-hexylindole-2,3-dione as an orange-red solid (yield: 74%). ¹H NMR (400 MHz, Chloroform-d) δ 7.72 (d, J = 9.8 Hz, 2H), 6.83 (d, J = 8.1 Hz, 1H), 3.79 - 3.63 (m, 2H), 1.76 - 1.64 (m, 2H), 1.34 (s, 6H), 0.93 - 0.88 (m, 3H).

5-Bromo-1-hexylindole-2-one: 5-bromo-1-hexylindole-2,3-dione (10.2 g, 32.88 mmol), 1,2-diethoxyethane (50 mL), and hydrazine hydrate (150 mL) were added into flask and refluxed at 100°C under nitrogen atmosphere for 40 h. After cooling to room temperature, the resulting mixture was poured into water and extracted with DCM three times. The organic phases were dried over anhydrous potassium sulfate, filtered, and evaporated to yield a brown solid. The crude product was further purified through column chromatography (eluent: petroleum ether) to obtain a yellow solid (yield: 92%). ¹H NMR (400 MHz, Chloroform-d) δ 7.41 (dd, J = 11.4,

3.2 Hz, 2H), 6.72 (d, $J = 8.2$ Hz, 1H), 3.69 (t, $J = 7.4$ Hz, 2H), 3.53 (s, 2H), 1.68 - 1.63 (m, 2H), 1.41 - 1.28 (m, 6H), 0.96 - 0.84 (m, 3H)

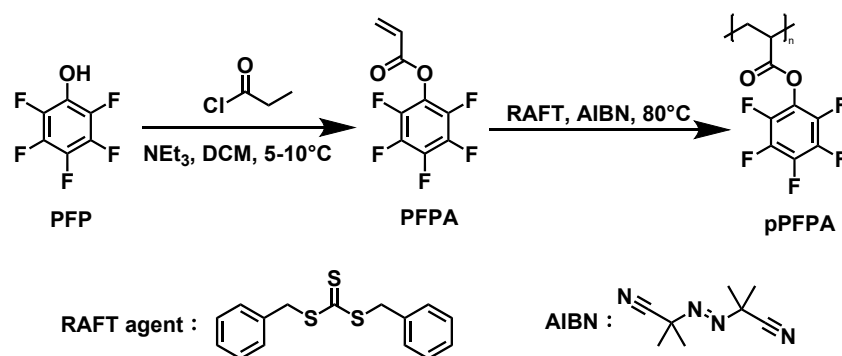
5-TAT: 5-Bromo-1-hexylindole-2-one (9.0 g, 30.38 mmol) was mixed with 100 mL of phosphorus oxychloride in a 250 mL flask. The resultant mixture was refluxed at 100°C under a nitrogen atmosphere for 12 h. After cooling to room temperature, the mixture was added dropwise to a mixture of deionized water and ethyl acetate. Subsequently, 8 M sodium hydroxide aqueous solution was slowly dripped into the solution until reaching pH=8. The resulting solution was extracted with DCM three times. The combined organic phases were dried over anhydrous potassium sulfate, filtered, and evaporated to dryness. The crude product was further purified through column chromatography to give 5-TAT as a white solid (yield: 93%). ^1H NMR (400 MHz, Chloroform- d) δ 8.23 (d, $J = 1.4$ Hz, 3H), 7.52 (dd, $J = 8.6, 1.5$ Hz, 3H), 7.42 (d, $J = 8.6$ Hz, 3H), 4.74 - 4.54 (m, 6H), 1.97 (q, $J = 11.7, 8.1$ Hz, 6H), 1.38 - 1.24 (m, 18H), 0.84 (t, $J = 7.0$ Hz, 9H)

5-PATAT: 5-TAT (0.5 g, 0.60 mmol), S1 (0.857 g, 2.70 mmol), potassium carbonate (1.0 g, 7.25 mmol), and tetrahydrofuran (THF, 30 mL), and water (3 mL) were stirred in a 100 mL flask. The flask was degassed and recharged with N_2 for three times before and after the addition of $\text{Pd}(\text{PPh}_3)_4$ (35 mg, 0.03 mmol), followed by stirring at 90°C for 2 days. After the reaction, 100 mL of water was added, and extracted with DCM for three times. The organic phases were combined, dried over anhydrous potassium sulfate, and filtered. The solvent was evaporated to obtain a black oily liquid. The crude product was purified on a silica gel column (eluent: ethyl acetate and petroleum ether (1/10-1/5, v/v)), resulting in a white solid (yield: 85%). ^1H NMR (400 MHz, Chloroform- d) δ 8.46 (d, $J = 8.3$ Hz, 3H), 8.27 (s, 3H), 7.71 (d, $J = 8.4$ Hz, 3H), 7.44 (dd, $J = 14.9, 7.8$ Hz, 9H), 7.35 (s, 3H), 7.23 (d, $J = 7.4$ Hz, 3H), 4.93 - 4.83 (m, 6H), 2.14 (t, $J = 7.5$ Hz, 6H), 2.06 (s, 6H), 1.57 - 1.48 (m, 6H), 1.23 - 1.04 (m, 30H), 0.77 - 0.69 (m, 18H).

PTF2: 5-TATAT (0.3 g, 0.26 mmol), phosphorus oxychloride (20 mL), and P_2O_5 (1.1 g) were stirred at 110 °C for 20 h. After that, the reaction mixture was slowly poured into a mixture of ice water and ethyl acetate (5/2). Sodium hydroxide solution (8 M) was then slowly added dropwise to pH = 9 and extracted with DCM for three times. The organic phases were combined and dried over anhydrous potassium sulfate. After filtration and solvent evaporation, the crude product was purified on a silica gel column (eluent: dichloromethane and petroleum ether (1/1,

v/v)) to give F2(yield: 83%). ^1H NMR (400 MHz, Chloroform- d , δ): 9.01 (s, 3H), 8.40 (d, J = 8.0 Hz, 3H), 8.24 (d, J = 8.0 Hz, 3H), 7.84 (s, 3H), 7.75 (t, J = 7.2 Hz, 3H), 7.60 (t, J = 7.4 Hz, 3H), 4.51 (t, J = 7.2 Hz, 6H), 3.24 (t, J = 7.9 Hz, 6H), 1.97 - 1.89 (m, 12H), 1.54 - 1.47 (m, 6H), 1.43 - 1.34 (m, 6H), 1.05 - 0.99 (m, 18H), 0.93 (t, J = 7.2 Hz, 9H), 0.64 (t, J = 7.0 Hz, 9H). ^{13}C (400 MHz, Chloroform- d , δ): 161.93, 142.96, 142.75, 140.90, 129.97, 127.61, 126.56, 126.23, 125.98, 124.34, 121.73, 120.96, 113.73, 105.68, 102.32, 47.46, 36.88, 32.44, 31.47, 29.92, 29.44, 26.66, 22.70, 22.53, 14.17, 13.79. MALDI-TOF MS $\text{C}_{78}\text{H}_{90}\text{N}_6$ m/z : Calcd. For $[\text{M}]^+$, exact mass: 1110.72, Found: 1111.496 $[\text{M}+\text{H}]^+$

2.2 Synthesis of polymers

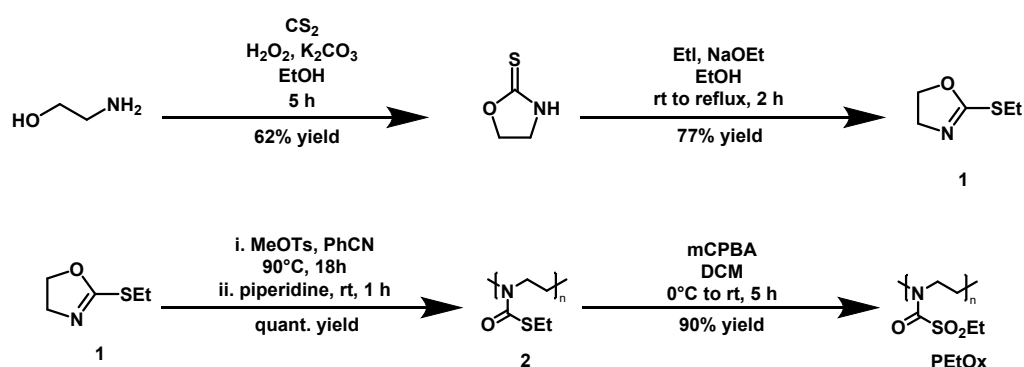


Scheme S2. Synthesis routes of **PFPA** and **pPFPA**

PFPA: A phenol derivative (30 mmol, Scheme S2) and triethylamine (45 mmol) were dissolved in dichloromethane at 0-5°C. Acryloyl chloride (30 mmol) was then added dropwise into the solution. The mixture was stirred at 5-10°C for 2 h, followed by stirring at room temperature overnight. After the reaction, 100 mL of saturated NaCl solution was added, and extracted with DCM for five times. Subsequently, the organic phase was dried over anhydrous potassium sulfate, filtered, and evaporated to dryness. Further purification was carried out on a silica gel column, resulting in the isolation of the corresponding aryl ester monomer. PFPA: ^1H NMR (400 MHz, Chloroform- d , δ): 6.71 (d, J = 17.3 Hz, 1H), 6.36 (dd, J = 17.3, 10.5 Hz, 1H), 6.17 (d, J = 10.5 Hz, 1H). ^{19}F NMR (376 MHz, Chloroform- d , δ): 152.66 - 153.17 (m), 158.42 (td, J = 21.4, 5.1 Hz), 162.79 (ddd, J = 21.8, 17.1, 5.0 Hz). Phenyl acrylate: ^1H NMR (400 MHz,

Chloroform-d, δ) 7.52 - 7.38 (m, 2H), 7.33 - 7.24 (m, 1H), 7.23 - 7.13 (m, 2H), 6.65 (dd, $J = 17.3, 1.3$ Hz, 1H), 6.37 (dd, $J = 17.3, 10.4$ Hz, 1H), 6.04 (dd, $J = 10.5, 1.3$ Hz, 1H).

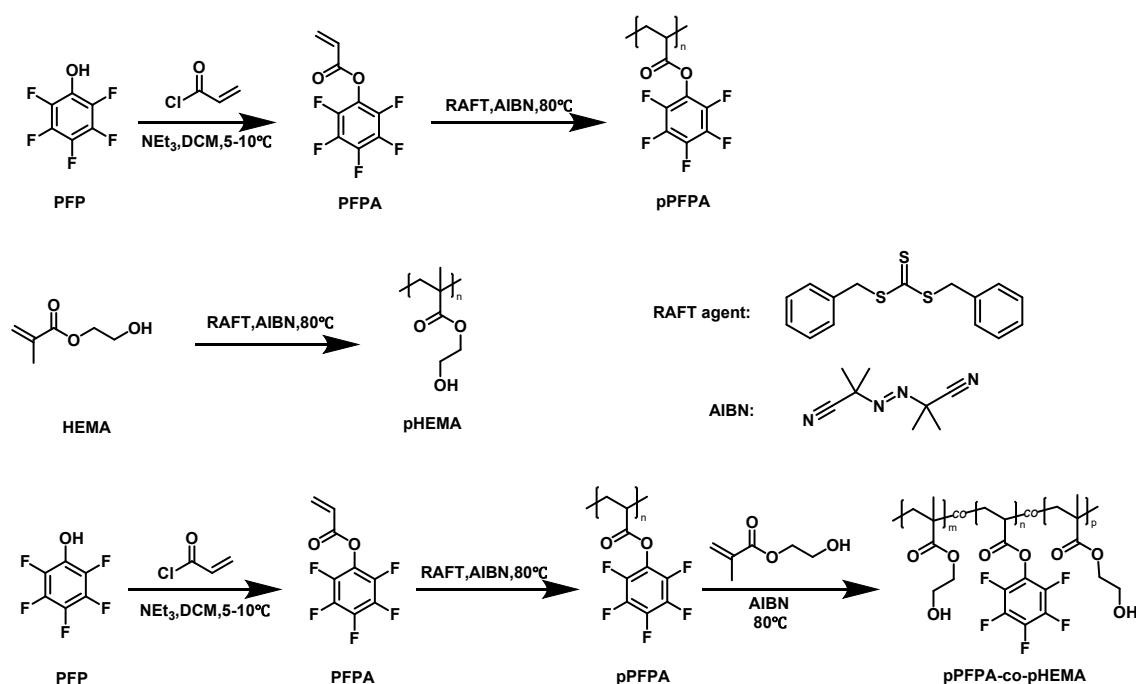
poly(pentafluoro-phenylacrylate) pPFPA: The mixture of monomer (40 mmol), benzyl dithiocarbamate (0.04 mmol, RAFT agent), AIBN (0.06 mmol), and 1,4-dioxane (20 mL) were stirred at 80°C for 35 h under a nitrogen atmosphere. Following this, the mixture was cooled to room temperature and gradually added dropwise into n-hexane. The resulting precipitate was dissolved and reprecipitated three times. Subsequently, the polymer was dried via vacuum drying at 40°C (yield: 75% - 81%).



Scheme S3. The route of PEtOx

Synthesis of PEtOx: PEtOx was synthesized according to previous research (*Adv. Mater.* **2023**, 35, 2303641). Specifically, Ethanolamine (6.04 mL, 100 mmol, 1 eq), ethanol (250 mL), carbon disulfide (12.03 mL, 200 mmol, 2 eq.) and potassium carbonate (6.90 g, 50 mmol, 0.5 eq.) were added into flask. Subsequently, 30% hydrogen peroxide solution (16 mL, 150 mmol, 1.5 eq.) was added dropwise within 1 hour and stirred for 4 h. After that, it was cooled to room temperature. The precipitate was removed by filtration. Saturated NaCl solution was added and extracted with ethyl acetate for 3 times. After that, the organic phase was dried over anhydrous sodium sulfate, filtered, and then evaporated. The crude product was recrystallized twice from ethanol, yielding colorless crystals of thiadiazolane-2-thione. Thiadiazolane-2-thione (18.21 g, 176.6 mmol, 1 eq.), ethanol sodium (21% in EtOH; 69 mL, 185 mmol, 1.05 eq.), iodoethane (21.3 mL, 263 mmol, 1.5 eq.) were dissolved in 600 mL of ethanol and then refluxed for 1 hour. Saturated sodium bicarbonate solution was added and extracted by dichloromethane for three

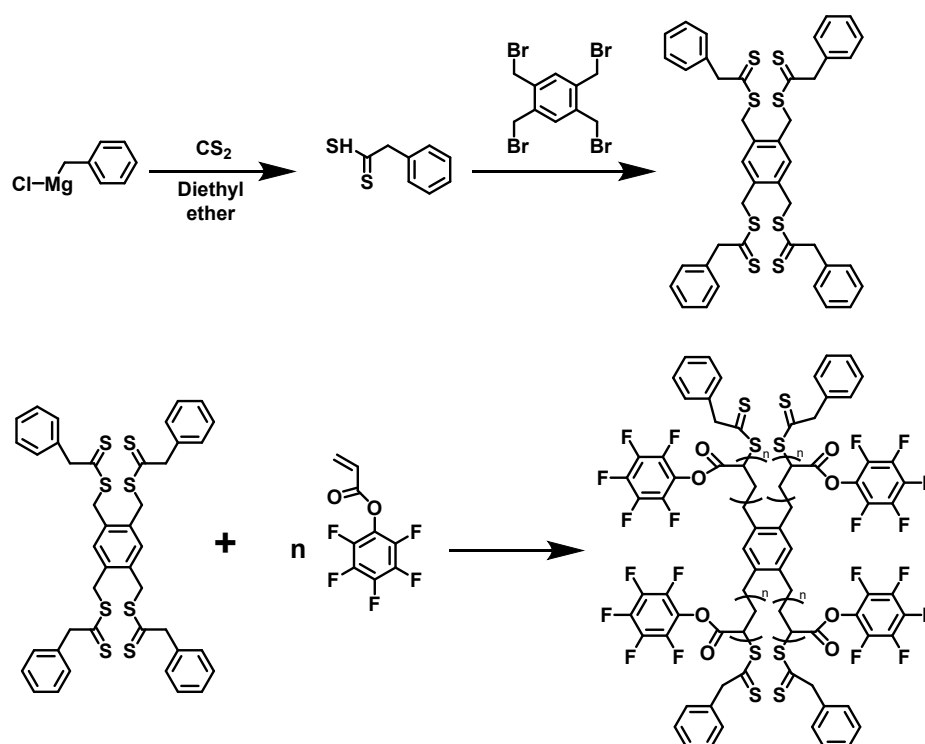
times. The organic phases were combined and washed with NaCl solution for 3 times, dried over anhydrous magnesium sulfate, filtered, and evaporated to obtain a light reddish-brown oily substance. To further purification, it was mixed and stirred overnight with freshly ground calcium hydride, followed by distillation under reduced pressure using a fractionation column, resulting in a colorless liquid (Scheme S3, compound 1). Subsequently, compound 1 (3.00 mL, 25.62 mmol, 200 eq.), benzyl cyanide (24 mL), and methyl trifluoromethanesulfonate (19.3 μ L, 0.128 mmol, 1 eq.) were added and stirred at 90°C for 18 h under a nitrogen atmosphere. The reaction mixture was precipitated in n-hexane. The sediment was collected, and then vacuum-dried at 60°C to obtain a colorless compound 2 (Scheme S3). Compound 2 (3.37 g, 25.7 mmol, 1 eq.) was dissolved in 85 mL of DCM and cooled in an ice bath. Subsequently, 100 mL of meta-chloroperoxybenzoic acid (12.10 g, 54 mmol, 2.1 eq.) was added dropwise. The temperature was then raised to room temperature, and the mixture was stirred for 5 h. The resulting solution was precipitated in ether, the solid was collected by filtration, and washed multiple times with ether. After vacuum drying, a white powder of PEtOx was obtained. ^1H NMR (400 MHz, Chloroform-d) δ 4.00 (s, 2H), 3.73 (s, 2H), 3.43 - 3.25 (m, 2H), 1.39 (t, J = 7.4 Hz, 3H).



Scheme S4. Synthesis routes of pPFPA-co-pHEMA

Synthesis of pPFPA-co-pHEMA: Under a nitrogen atmosphere, 4 g of PFPA (16.8 mmol), 12.2 mg of benzyl trithiocarbonate RAFT agent (4.16 mmol), 4 mg of AIBN (0.0244 mmol), and 10 mL of 1,4-dioxane were mixed. The reaction was carried out for 24 h at 80°C.

Then, 0.43 g of hydroxyethyl methacrylate (HEMA) (3.36 mmol) and 0.8 mg of AIBN were added, with pPFPA used as the chain transfer agent, and the reaction continued under nitrogen for another 24 h. After the reaction was completed, oxygen was introduced to stop the polymerization. The product was purified using a dissolution-precipitation method with cold ether. The resulting product was the amphiphilic block copolymer pPFPA-co-pHEMA, and the block ratio was determined by NMR spectroscopy.



Scheme S5. Synthesis routes of **star polymer**

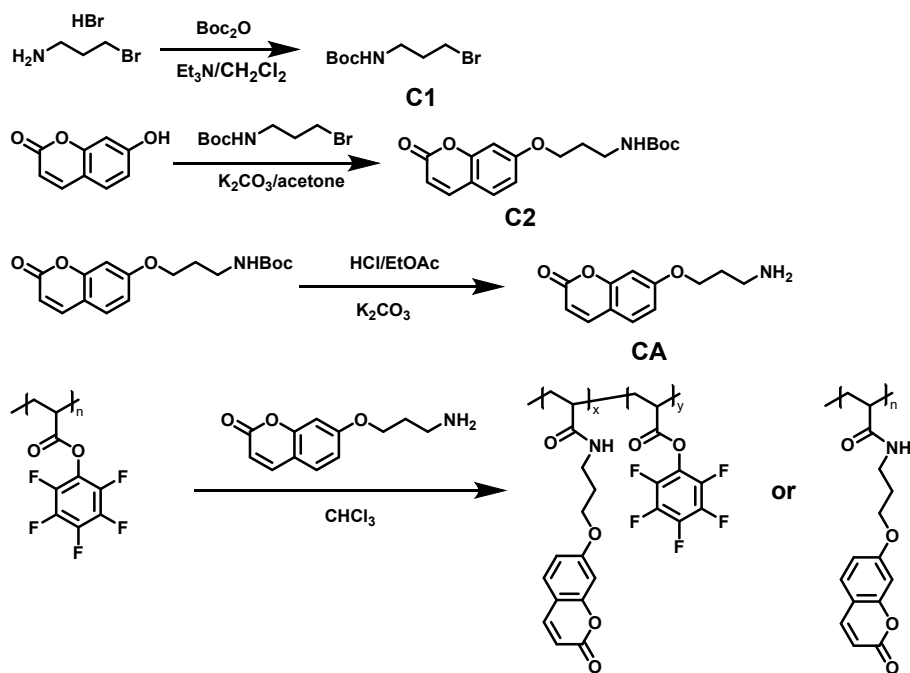
The star polymer was synthesized according to our previous study (*Adv. Mater.* **2023**, 35, 2303641)^[2]. The specific procedures are shown as follows:

Synthesis of a Four-Arm RAFT Agent:First, 0.32 mol of benzylmagnesium chloride and 0.33 mol of carbon disulfide were added to 30 mL of anhydrous ether. The mixture was stirred at 0°C under a nitrogen atmosphere for 3 h. After the reaction was complete, the reaction mixture

was slowly poured into 200 mL of ice water. The mixture was washed several times with ether, and the aqueous phase was collected. The pH was adjusted to 2 using 10% precooled hydrochloric acid, and then the mixture was extracted three times with ether. After collecting the organic phases, the solution was dried over anhydrous sodium sulfate, and the solvent was evaporated under vacuum, yielding an orange oily product, 2-phenylethanedithiolate.

An equimolar amount of potassium hydroxide (1.1 eq.) was weighed and dissolved in a minimal amount of distilled water. It was mixed with 2-phenylethanedithiolate, and any residual water was removed under vacuum, resulting in an orange powder of 2-phenylethanedithiolate (1.1 eq). This product was dissolved in anhydrous tetrahydrofuran (THF) and 1,2,4,5-tetrabromomethylbenzene (1 eq.) was added. The mixture was refluxed under a nitrogen atmosphere for 1 hour. After the reaction was complete, water was added and the product was extracted with toluene. The solvent was evaporated, yielding a yellow solid, which was recrystallized from an equal volume of ethanol and chloroform. The structure of the product was confirmed by ^1H NMR (400 MHz, Chloroform- d): δ 7.42 - 6.95 (m, 23H), 4.27 (d, J = 4.9 Hz, 8H), 3.72 (q, J = 7.0 Hz, 8H).

Synthesis of the Final Product: Then, 10 g of PFPA (0.042 mol), 83 mg of the four-arm RAFT agent (10.4 mmol), and 10 mg of AIBN (0.061 mmol) were weighed and added to a 100 mL single-neck round-bottom flask. To this, 30 mL of 1,4-dioxane was added. The reaction was carried out under nitrogen at 80°C for 60 h. After the reaction was complete, the mixture was cooled to room temperature, and the reaction solution was slowly added dropwise to n-hexane to precipitate the product. The precipitate was repeatedly dissolved in tetrahydrofuran, and the white solid was collected by centrifugation and vacuum-dried at 25-40°C.



Scheme S6. Synthesis routes of **linear coumarin polymer**

Synthesis of linear coumarin polymer:

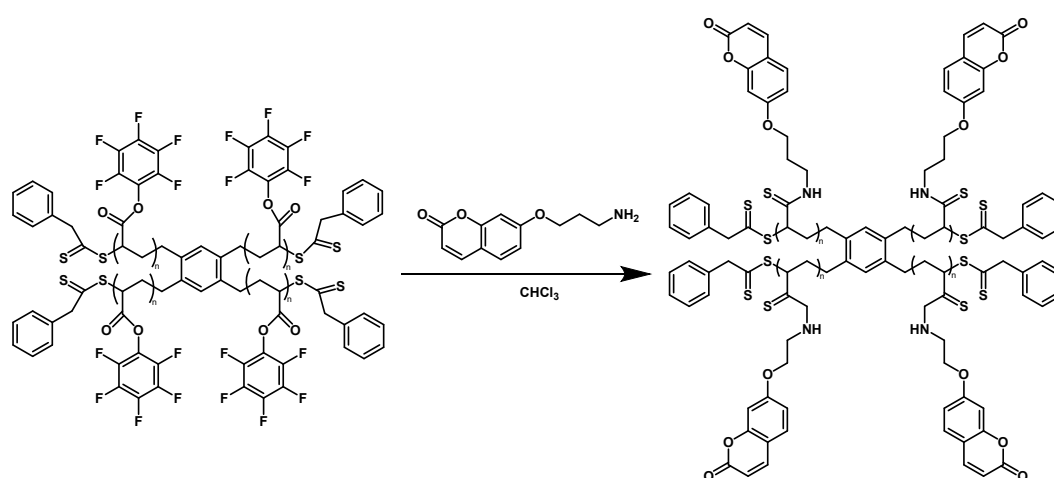
C1: First, 3.28 g of 3-bromopropylamine hydrobromide (0.015 mol) was added to 20 mL of dichloromethane, where the solid was slightly soluble. Under a nitrogen atmosphere, 4.2 mL of triethylamine was slowly added dropwise at 0°C while stirring for 30 minutes. After the solid completely dissolved, 3.44 g of di-tert-butyl dicarbonate (0.015 mol) was slowly added, and the mixture was stirred overnight. After the reaction was complete, deionized water was added, and the mixture was extracted using a 250 mL separatory funnel. The organic phase was collected, dried over anhydrous sodium sulfate, and the solvent was concentrated under vacuum to obtain a light yellow oily product, **C1**. The structure of **C1** was confirmed by ^1H NMR (400 MHz, Chloroform- d): δ 4.72 (s, 1H), 3.45 (t, $J = 6.5$ Hz, 2H), 3.28 (q, $J = 6.4$ Hz, 2H), 2.05 (p, $J = 6.7$ Hz, 2H), 1.44 (s, 9H).

C2: Next, 1.2 g of **C1** (5.6 mmol), 0.76 g of 7-hydroxycoumarin (4.6 mmol), 1.04 g of anhydrous potassium carbonate (9.4 mmol), and 30 mL of anhydrous acetone were placed into a 100 mL round-bottom flask, and the mixture was refluxed for 24 h. After the reaction was complete, the solvent was evaporated, and the product was extracted using dichloromethane and saturated brine. The organic phase was collected, dried, and concentrated to yield a yellow

oily product. The crude product was purified by silica gel column chromatography (eluent: dichloromethane/petroleum ether, v/v, 3/1), and the final product, C2, was obtained as a yellow solid. The structure of C2 was confirmed by ^1H NMR (400 MHz, Chloroform- d): δ 7.65 (d, J = 9.4 Hz, 1H), 7.37 (d, J = 8.6 Hz, 1H), 6.89 - 6.76 (m, 2H), 6.25 (dd, J = 9.5, 2.4 Hz, 1H), 4.86 (s, 1H), 4.08 (t, J = 6.0 Hz, 2H), 3.35 (q, J = 6.6 Hz, 2H), 2.10 - 1.96 (m, 2H), 1.44 (d, J = 2.1 Hz, 10H).

CA: Then, 1.38 g of C2 was added to 3.4 mL of ethyl acetate, and 4 mL of HCl was slowly added dropwise. The mixture was stirred overnight. After the reaction was complete, the precipitate was filtered off, and the filtrate was washed several times with 5% potassium carbonate solution. The solvent was evaporated, and the product was vacuum-dried at room temperature to obtain a yellow solid powder, CA. The structure of CA was confirmed by ^1H NMR (400 MHz, Chloroform- d): δ 7.64 (d, J = 9.5 Hz, 1H), 7.37 (d, J = 8.4 Hz, 1H), 6.88 - 6.78 (m, 2H), 6.25 (d, J = 9.5 Hz, 1H), 4.12 (t, J = 6.1 Hz, 2H), 2.94 (t, J = 6.8 Hz, 2H), 1.97 (t, J = 6.4 Hz, 2H).

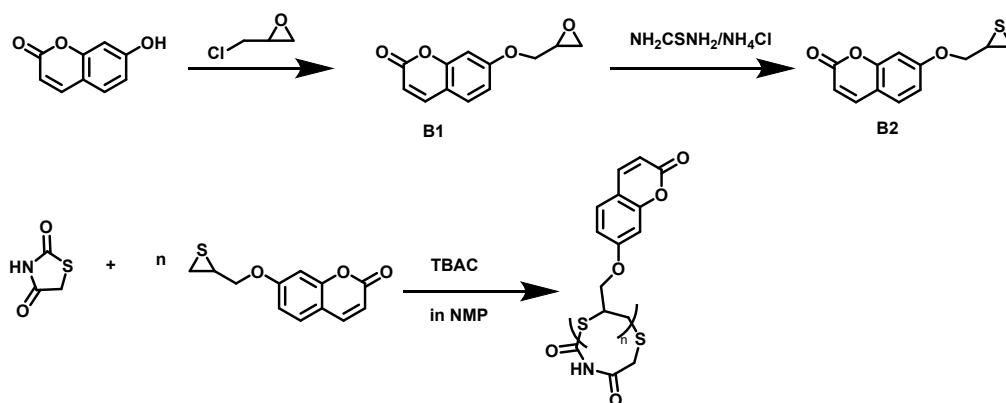
Finally, based on the amination reaction between pPFPA and the alkylamine derivative, pPFPA and CA were mixed and dissolved in chloroform. The mixture was stirred thoroughly, allowing the pentafluorophenyl ester group on the pPFPA chain to be replaced by CA. By adjusting the molar ratio, different CA-substituted pPFPA could be obtained. The monomer ratio in the polymer was calculated by NMR spectroscopy. If CA was in excess, linear coumarin polymers could be obtained.



Scheme S7. Synthesis routes of the star-shaped coumarin polymer

Synthesis of Star-Shaped Coumarin Polymer:

Similar to the synthesis route of the linear coumarin polymer, excess CA was mixed with the star-shaped polymer and dissolved in chloroform. The mixture was stirred thoroughly, and the pentafluorophenyl ester groups on the arms of the star-shaped polymer were replaced, resulting in the star-shaped coumarin polymer.



Scheme S8. Synthesis routes of the Cyclic coumarin polymer

Synthesis of Cyclic Coumarin polymer:

B1: First, 0.58 g of 7-hydroxycoumarin (3.6 mmol), 4.75 g of epichlorohydrin (51.3 mmol), and 0.25 g of potassium hydroxide (4.5 mmol) were added to a 100 mL round-bottom flask. Ethanol was added, and the mixture was heated to 78°C and refluxed for 5 h. After the reaction was complete, as indicated by TLC, the reaction was stopped, and the mixture was cooled to room temperature. The solvent was evaporated by rotary evaporation, and the filtrate was dried. The product was separated by silica gel column chromatography to obtain a white solid powder, B1. The structure of B1 was confirmed by ¹H NMR (400 MHz, Chloroform-d): δ 7.65 (d, J = 9.5 Hz, 1H), 7.39 (d, J = 8.6 Hz, 1H), 6.98 - 6.75 (m, 2H), 6.27 (d, J = 9.5 Hz, 1H), 4.34 (dd, J = 11.0, 2.8 Hz, 1H), 3.97 (dd, J = 11.0, 6.0 Hz, 1H), 3.39 (ddd, J = 6.0, 2.9, 1.4 Hz, 1H), 2.95 (dd, J = 4.8, 4.1 Hz, 1H), 2.80 (dd, J = 4.9, 2.7 Hz, 1H).

B2: Next, 2 g of B1 (9.17 mmol), 1.4 g of thiourea (18.42 mmol), and 2 g of ammonium chloride (37.38 mmol) were added to a 100 mL round-bottom flask. A small amount of methanol was added, and the mixture was thoroughly mixed. The reaction was carried out in an oil bath at 60-

70°C for 75 minutes. The progress of the reaction was monitored by TLC, and after the reaction was complete, 50 mL of deionized water was added. The reaction mixture was extracted with DCM (3×50 mL). The organic phases were combined, dried, and concentrated. The product was separated by silica gel column chromatography to obtain a white solid powder, B2. The structure of B2 was confirmed by ^1H NMR (400 MHz, Chloroform- d): δ 7.64 (d, $J = 9.5$ Hz, 1H), 7.39 (d, $J = 8.6$ Hz, 1H), 6.90 – 6.78 (m, 2H), 6.27 (d, $J = 9.5$ Hz, 1H), 4.21 (dd, $J = 10.1$, 5.8 Hz, 1H), 4.03 (dd, $J = 10.1$, 6.7 Hz, 1H), 3.29 (p, $J = 6.0$ Hz, 1H), 2.64 (dt, $J = 6.2$, 1.0 Hz, 1H), 2.36 (dd, $J = 5.1$, 1.5 Hz, 1H).

Finally, 0.468 g of B2 (2.0 mmol), 0.0234 g of 2,4-thiazolidinedione (0.2 mmol), and 0.083 g of tetrabutylammonium chloride (0.3 mmol) were dissolved in N-methylpyrrolidone. The reaction tube was cooled, and the air was replaced with nitrogen, then sealed. The reaction was carried out at 60°C under nitrogen for 24 h. After the reaction was complete, a small amount of chloroform was added to dilute the reaction mixture, and methanol was slowly added to precipitate the solid. The solid was repeatedly dissolved and precipitated, then vacuum-dried at 25°C for 24 h. The final product, cyclic coumarin, with approximately 10 monomers, was obtained.

3. Supporting Figures and Tables

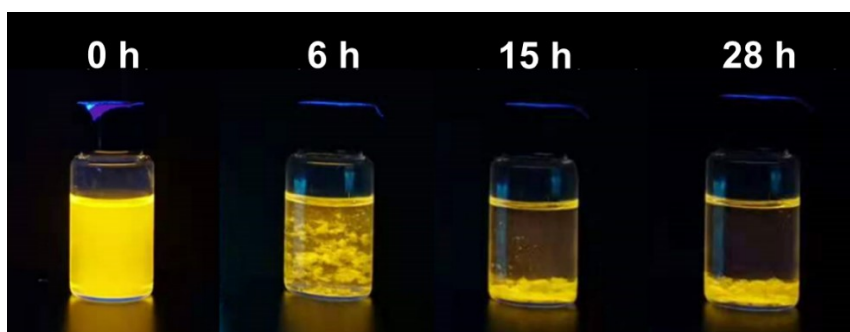


Figure S1. Fluorescence images of PTF2/pPFPA (1:2500) in THF/ toluene solution at 0 h, 6 h, 15 h, and 28 h.

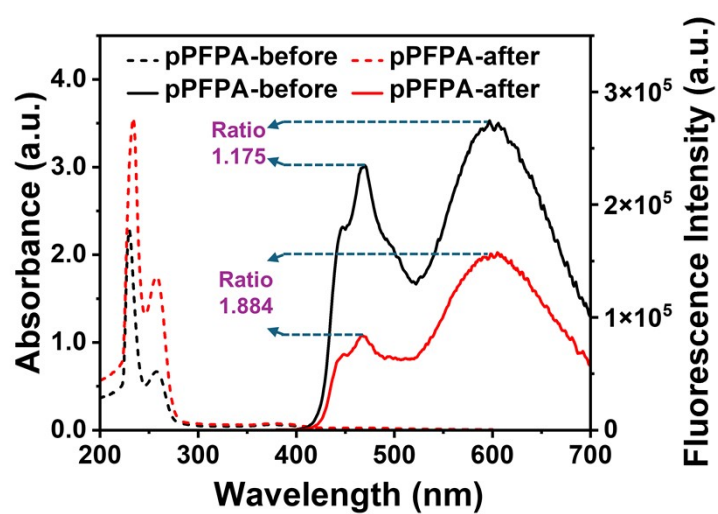


Figure S2. The fluorescence emission intensity ratio at 595 nm to 475 nm for the PTF2/PEtOx mixture in DCM before and after assembly.

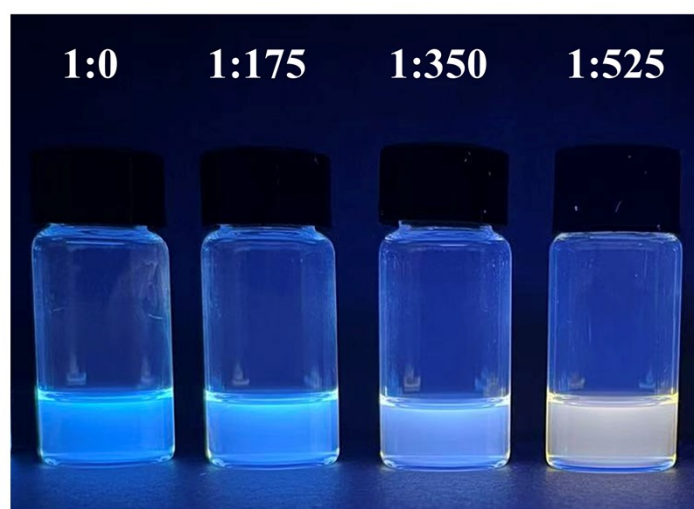


Figure S3. The fluorescence images of PTF2/PEtOx at different molar ratios in DCM.

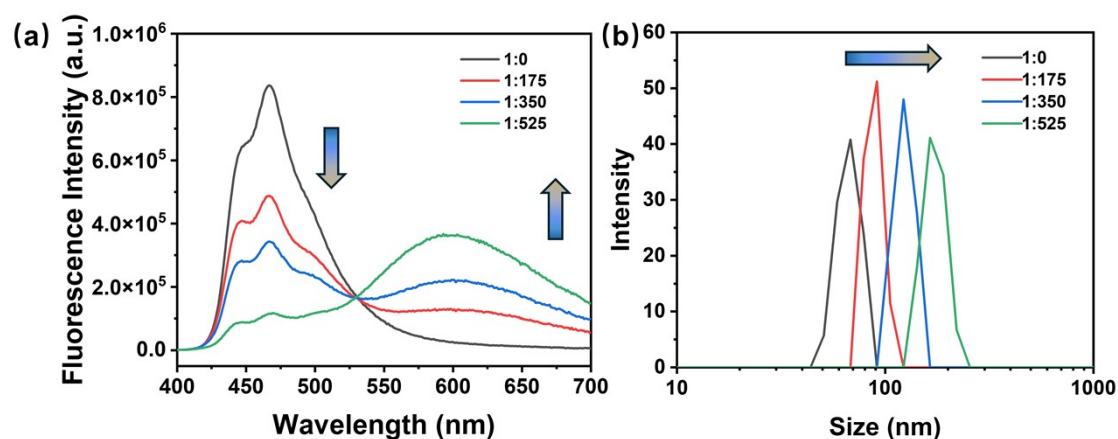


Figure S4. (a) Fluorescence emission spectra of PTF2/PEtOx at different molar ratios in DCM. (b) DLS characterizations of different molar ratios of PTF2/PEtOx in DCM.

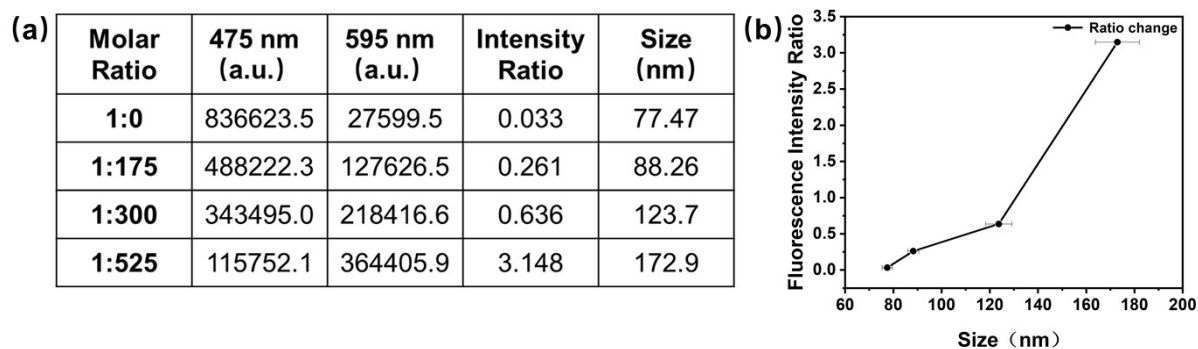


Figure S5. (a) The fluorescence emission intensity ratio at 595 nm/475 nm and particle size for different molar ratios of PTF2/PEtOx in DCM. (b) Correlation between the fluorescence emission intensity ratio at 595 nm/475 nm and the polymer particle size for different molar ratios of PTF2/PEtOx in DCM.

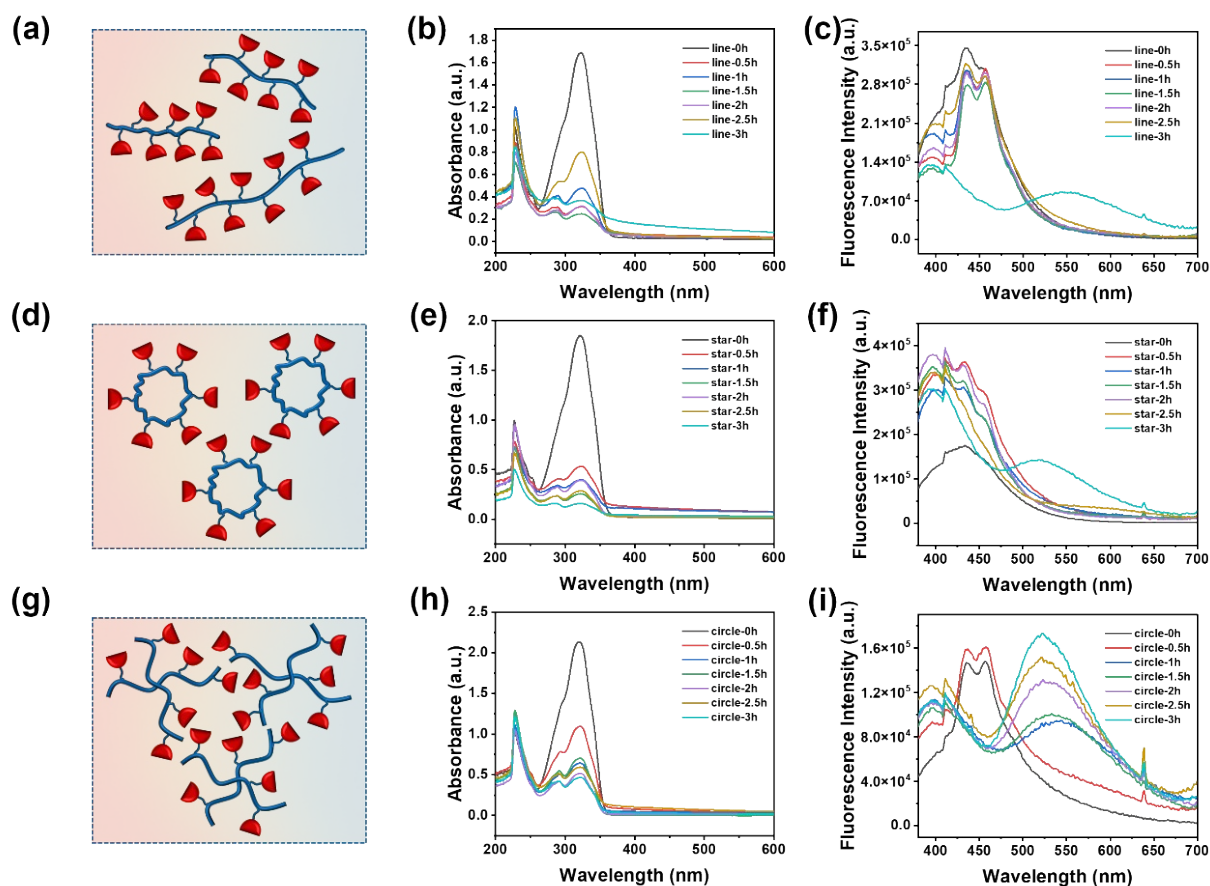


Figure S6. The UV-vis absorption and fluorescence emission spectra of linear (a-c), star (d-f), and circle coumarin polymers (g-i) after 365 nm light exposure for 0 h, 0.5 h, 1 h, 1.5 h, 2 h, 2.5 h, and 3 h, followed by the addition of the PTF2 fluorescent molecule.

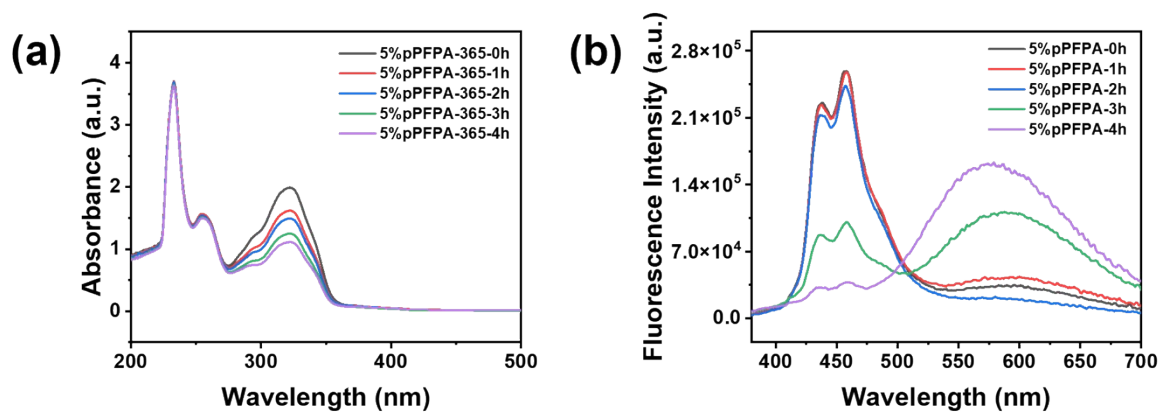


Figure S7. (a) Fluorescence emission and (b) UV-vis absorption spectra of 5% coumarin pPFPA.

Table S1. The fluorescence emission intensity ratio at 595 nm to 475 nm for the PTF2/PEtOx mixture in DCM before and after assembly.

Time (h)	475 nm (a.u.)	595 nm (a.u.)	Intensity Ratio
0	233580.7	274492.7	1.175
40	82956.2	156321.9	1.884

Table S2. Mn and PDI of polymers containing 5% coumarin irradiated by UV light at different times.

Sample	Mn	PDI
5% pPFPA-365 nm-0 h	7619	3.57
5% pPFPA-365 nm-4 h	10657	1.68
5% pPFPA-365 nm-8 h	12154	3.51
5% pPFPA-365 nm-10 h	12573	1.77
5% pPFPA-365 nm 10 h-254 nm 0 h	13882	1.67
5% pPFPA-365 nm 10 h-254 nm 1 h	10481	3.38
5% pPFPA-365 nm 10 h -254 nm 3 h	9802	1.86

4. NMR Spectra

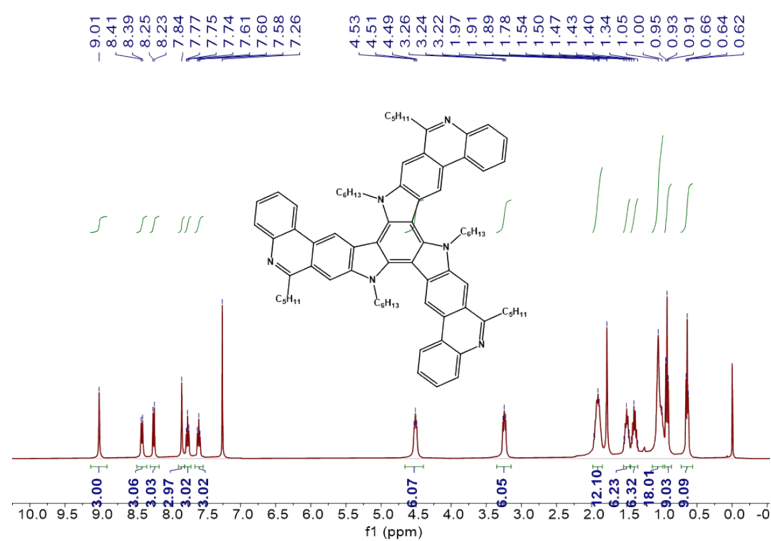


Figure S8. The ^1H NMR spectrum (400 MHz) of **PTF2** in CDCl_3 .

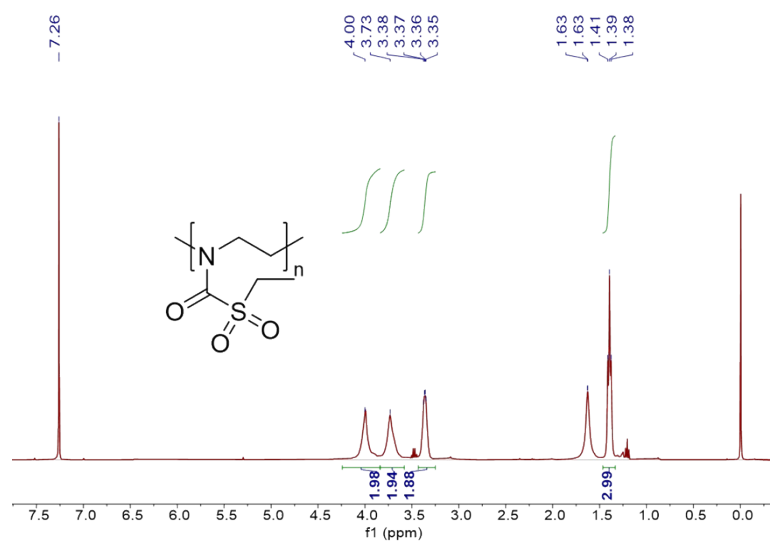


Figure S9. The ^1H NMR spectrum (400 MHz) of **PEtOx** in CDCl_3 .

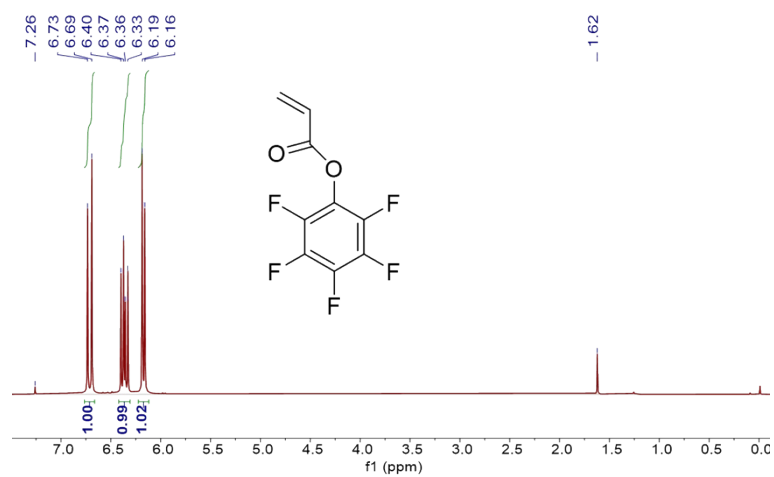


Figure S10. The ^1H NMR spectrum (400 MHz) of **PFPA** in CDCl_3 .

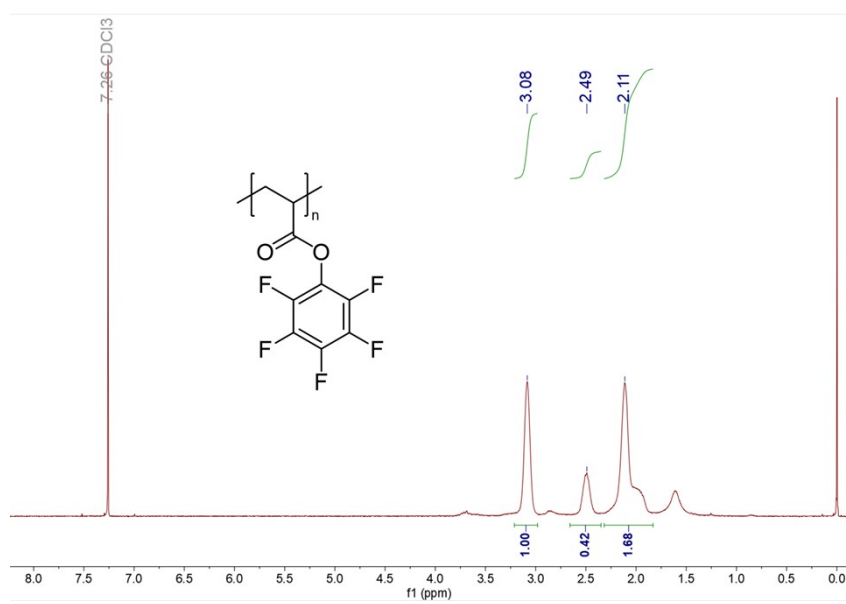


Figure S11. The ^1H NMR spectrum (400 MHz) of **pPFPA** in CDCl_3 .

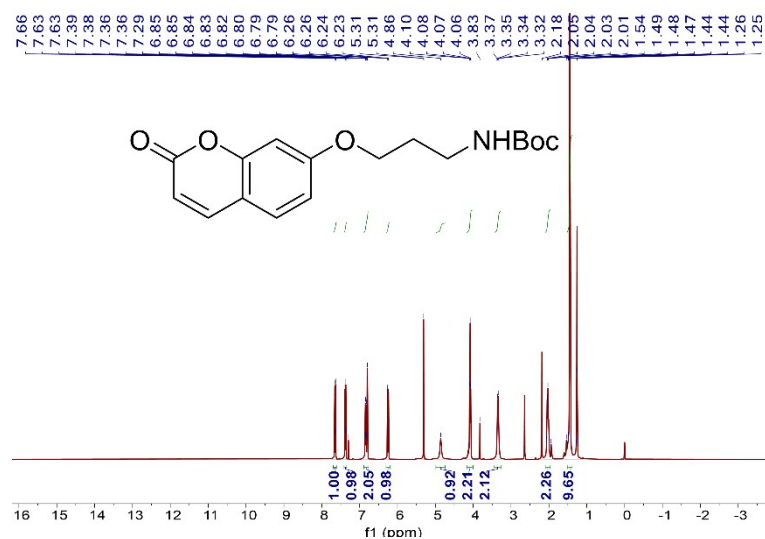


Figure S14. The ¹H NMR spectrum (400 MHz) of **C2** in CDCl₃.

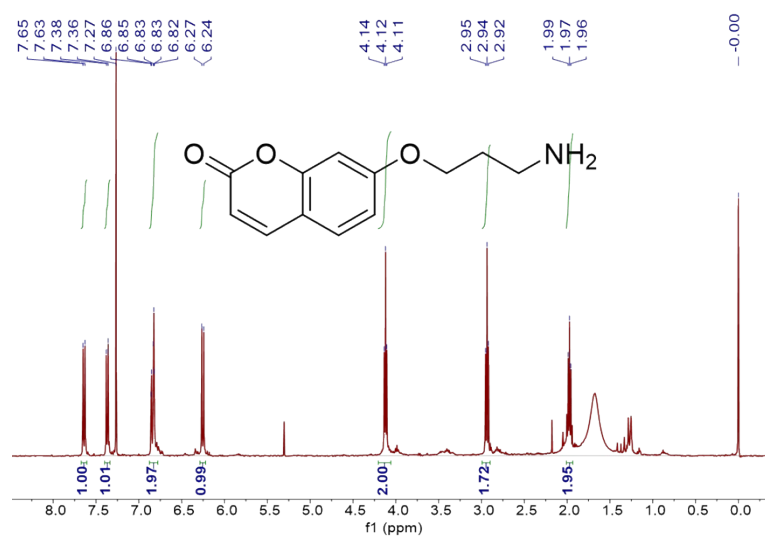


Figure S15. The ¹H NMR spectrum (400 MHz) of **CA** in CDCl₃.

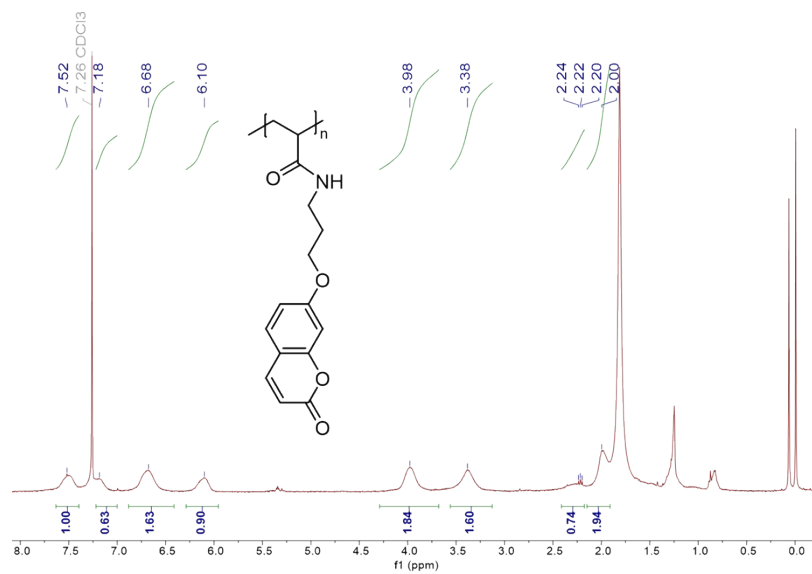


Figure S16. The ¹H NMR spectrum (400 MHz) of **Linear coumarin polymer** in CDCl₃.

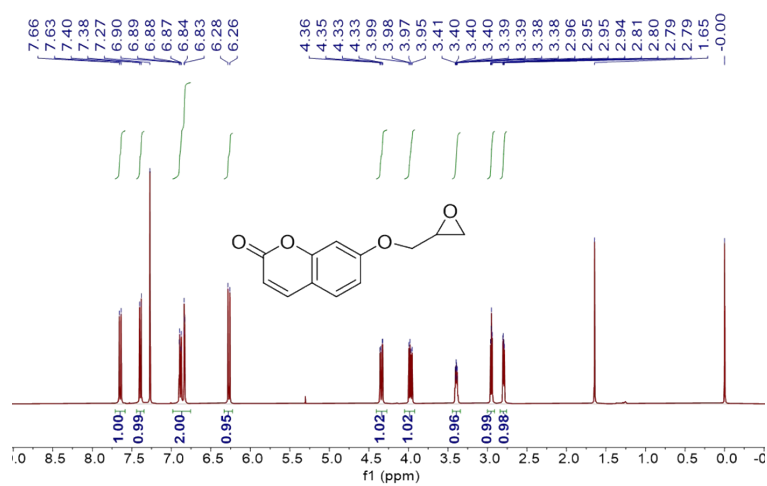


Figure S17. The ¹H NMR spectrum (400 MHz) of **B1** in CDCl₃.

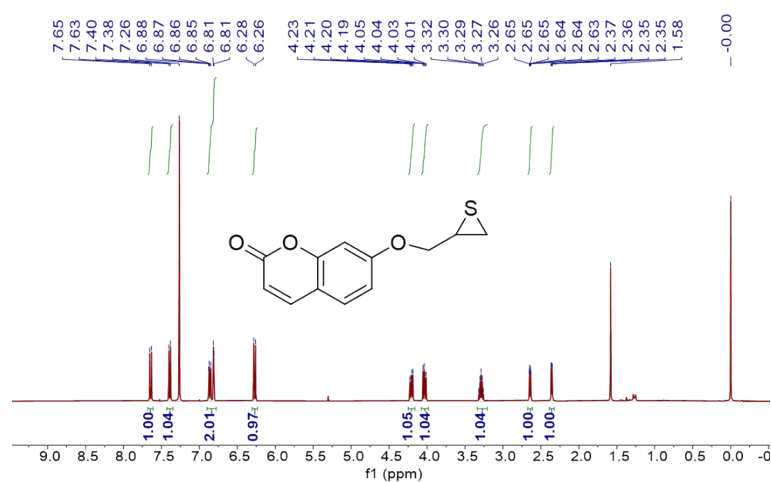


Figure S18. The ¹H NMR spectrum (400 MHz) of **B2** in CDCl₃.

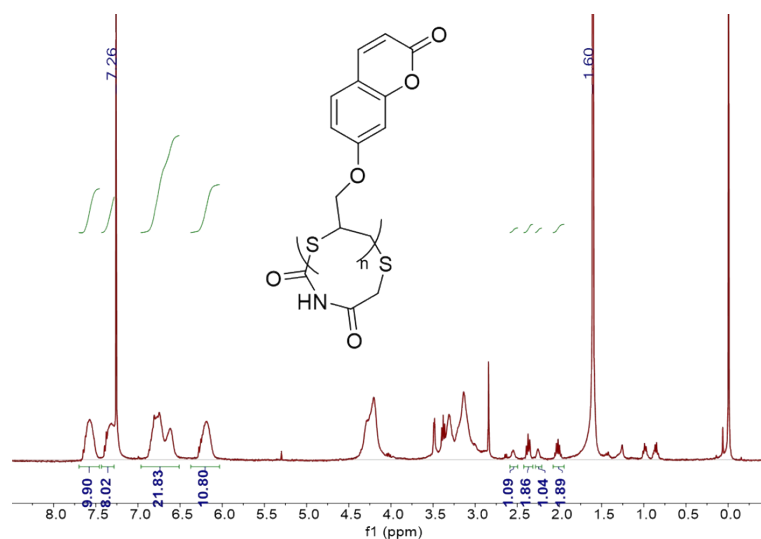


Figure S19. The ¹H NMR spectrum (400 MHz) of **Ring-shaped polymer** in CDCl₃.

References

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2. Y. Ling, J. Liu, Y. Dong, Y. Chen, J. Chen, X. Yu, B. Liang, X. Zhang, W. An, D. Wang, S. Feng and W. Huang, *Adv. Mater.*, 2023, **35**, e2303641.
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