Supporting information (SI)

Butterflyfish-inspired photo-responsive supramolecular fluorescence polymers for underwater anti-counterfeiting

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Materials and Methods

Materials

2,2,2-Trifluoroethylmethacrylate(TFEMA, 96%), 2,2,3,4,4,4-Hexafluorobutyl acrylate (HFBA, 96%), and phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (I-819，99%) were purchased from HEOWNS. TFEMA and HFBA were purified by column chromatography to remove the polymerization inhibitor before use. Unless other-wise stated, other all reagents were utilized from Energy Chemical as well as used without further purification. Distilled water was further purified by a Milli-Q system in all experiments. SDTE and BTBA were synthesized according to the reported methods[1].

Synthesis of non-fluorescent polymer (P0)

The solution of trimethylbenzaldehyde (10 mmol), HFBA (10 mmol), and I-819 (0.2 mmol) was irradiated by Vis light (40 mW/cm^2) for 1 h to get the sample. After the reaction is completed, the polymer is removed from the mold and dissolved with a small amount of dichloromethane, precipitate and dry in petroleum ether to obtain polymer **P0**.

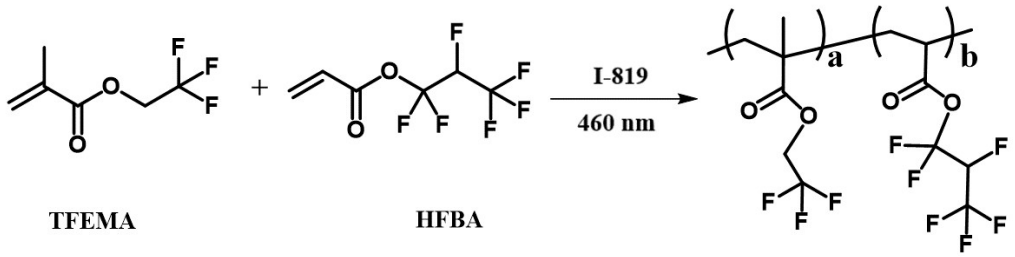

Figure S1. Synthesis of polymer **P0**.

Synthesis of non-fluorescent polymer (P1)

The solution of trimethylbenzaldehyde (10 mmol), HFBA (10 mmol), I-819 (0.2 mmol), and BTBA (8.18x10^{-2} mmol) was irradiated by Vis light (460 mW/cm^2) for 1 h to get the sample. After the reaction is completed, the polymer is removed from the mold and dissolved

with a small amount of dichloromethane, precipitate and dry in petroleum ether to obtain polymer **P1**.

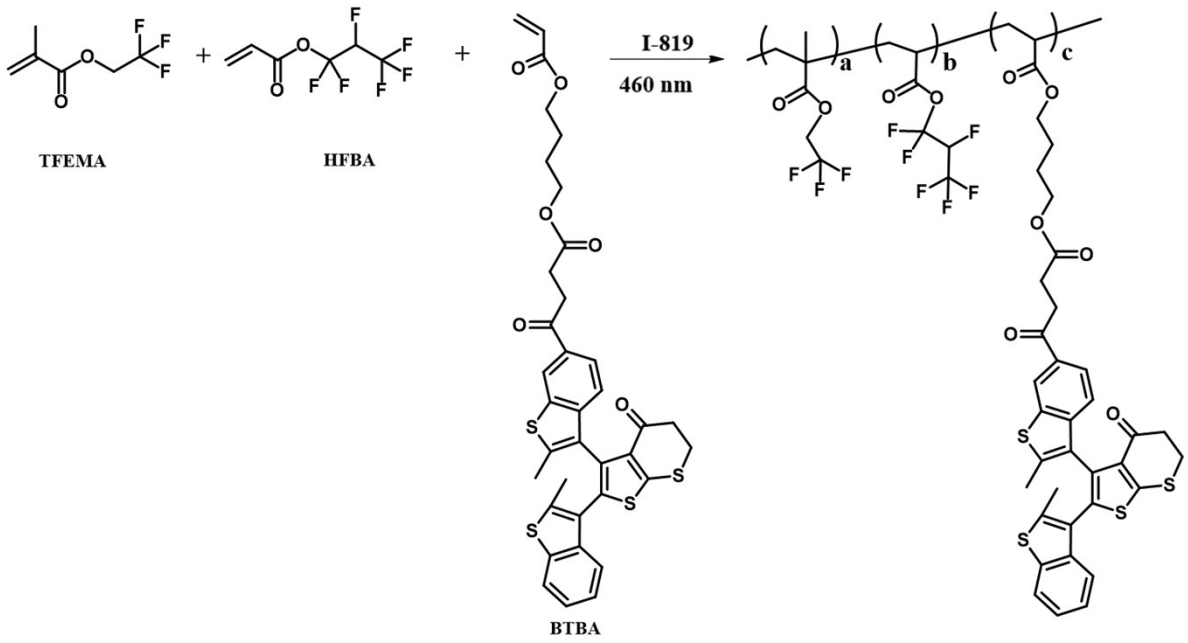

Figure S2. Synthesis of polymer **P1**.

Synthesis of non-fluorescent polymer (P2)

The solution of trimethylbenzaldehyde (10 mmol), HFBA (10 mmol), I-819 (0.2 mmol), and SDTE (6.36×10^{-2} mmol) was irradiated by Vis light (40 mW/cm^2) for 1 h to get the sample. After the reaction is completed, the polymer is removed from the mold and dissolved with a small amount of dichloromethane, precipitate and dry in petroleum ether to obtain polymer **P2**.

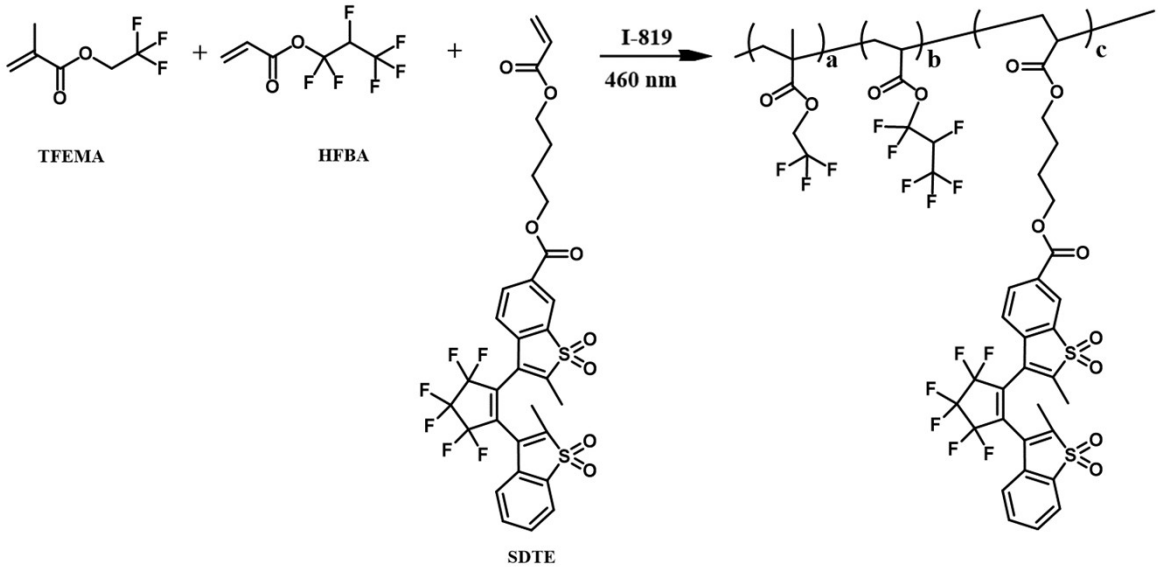

Figure S3. Synthesis of polymer **P2**.

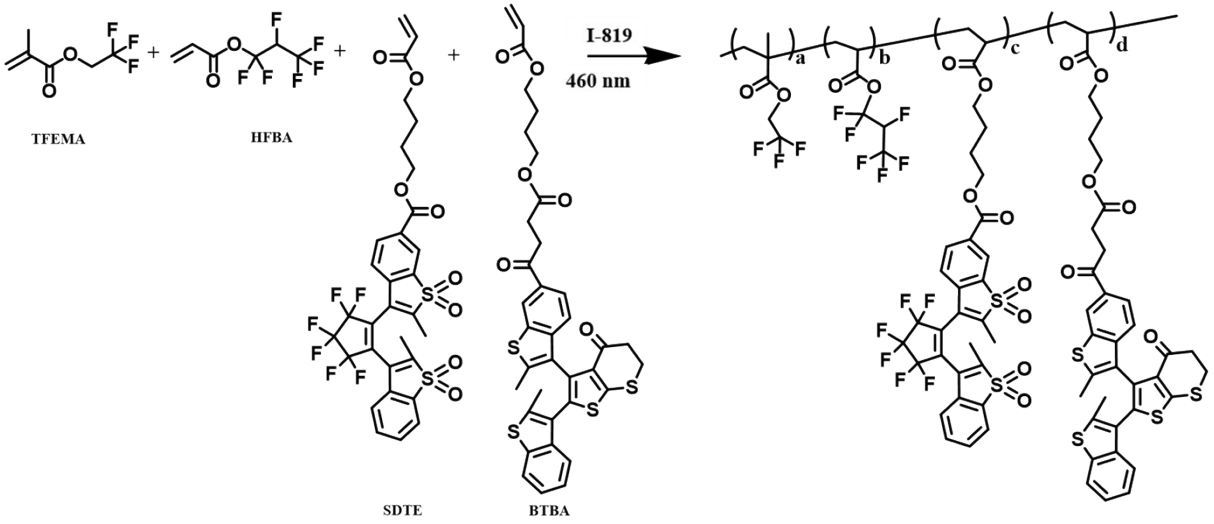

Figure S4. Synthesis of polymer **P3**.

Table S1. Composition and characteristics of the polymer samples.

Sample[a]	TFEMA feed [mg]	HFBA feed [mg]	I-819 feed [mg]	BTBA feed [mg]	SDTE feed [mg]	Mn[b] [kDa]	PDI[b]
P0	1680	2360	84.7	0	0	31.5	1.50
P1	1680	2360	84.7	56.3	0	32.9	1.53
P2	1680	2360	84.7	0	44.6	31.7	1.46
P3	1680	2360	84.7	56.3	44.6	27.4	1.54

Self-healing

P1, **P2** and **P3** were cut, respectively. The pieces were placed together to allow their surfaces contact in distilled water (25 °C) for 24 hours. Finally, the self-healing samples were obtained.

Acid, alkali, and salt resistance

P3 were immersed in the different solutions (pure water (pH=7.05), acid solution (HCl, pH = 1), and basic solution (NaOH, pH = 14), salt solution (26.5 wt%), seawater) for a week, and the shape of polymer block and fluorescence photographs were observed.

Antifouling

P3 were immersed in the mud and black ink for a week, and the contaminative sample were washed with water. The shape of polymer block and light-induced fluorescence photographs were observed.

Processability

The quadrate **P0** (4.2 g) was cut and dissolved into tetrahydrofuran (THF, 5 mL) to prepare the solutions. Subsequently, the solutions were poured into the mould (triangular body). The triangular body was obtained by the evaporation of THF at the room temperature. Next, the triangular body was further cut and placed in the mould (five-pointed star). Finally, a five-pointed star was prepared by heating at 100 °C.

Tensile tests and loading-unloading tests

Tensile mechanical properties were researched by the instron universal testing machine (Legend 2369) at room temperature. The size of the specimens is 20 × 3 × 1 mm. For the

grown sample with different thickness, its thickness is determined according to the actual thickness. The strain rate is 10 mm/min. The stress-extension ratio curves were automatically recorded using the universal tester.

Light-induced reversible fluorescence of artificial butterflyfish

According to the dye ratio of Fig. 5a, seven polymer blocks were prepared by light-induced polymerization, and the prepared polymer blocks were modified by customized aluminum alloy cutting molds to obtain A1-A7, and the incision surfaces of the seven parts of the butterfly fish were spliced, and finally the polymer had self-healing properties to obtain a complete photochromic butterflyfish model.

Underwater anti-counterfeiting

P0, **P1**, **P2**, **P3** four polymers can be prepared by photopolymerization, the prepared four polymers are placed in a 70 °C oven, waiting for them to soften into a fluid state, and then they are shaped with a PTFE mold and processed into a cube of 3×3×3 mm, according to the arrangement of Fig. 4a, the facets of the polymer blocks are in contact with each other, and the polymer has self-healing properties by using the polymer, and finally a polymer lattice with information encryption effect is obtained

Anti-counterfeiting labels

The prepared **P0**, **P1**, **P2**, **P3** four polymers are heated, and the customized PTFE mold is processed into 3×3×3 mm polymer blocks, because the polymer has good adhesion to the glass, the polymer is adhered to the glass of the diving goggle according to the arrangement of Fig. 5e and finally the underwater equipment label with anti-counterfeiting function is obtained

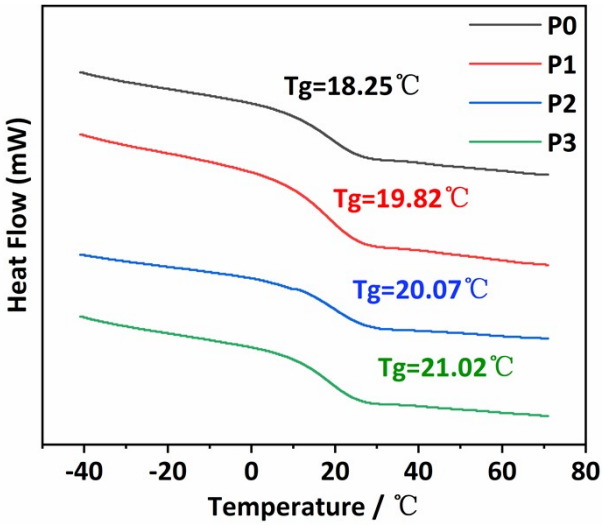

Figure S5. DSC of **P0**, **P1**, **P2**, and **P3**.

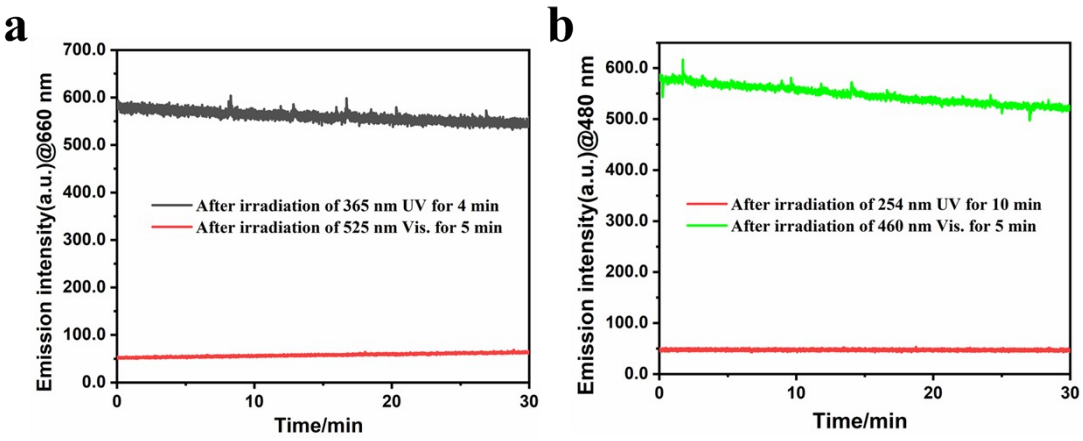

Figure S6. The photostability of **P1** (a) and **P2** (b) under continuous 410 nm light excitation. (a) **P1** used for meas urements were first irradiated by 525 nm visible light for 5 min, and then 365 nm UV light for 4 min. (b) **P2** used for measurements were first irradiated by 460 nm visible light for 5 min, and then 254 nm UV light for 10 min.

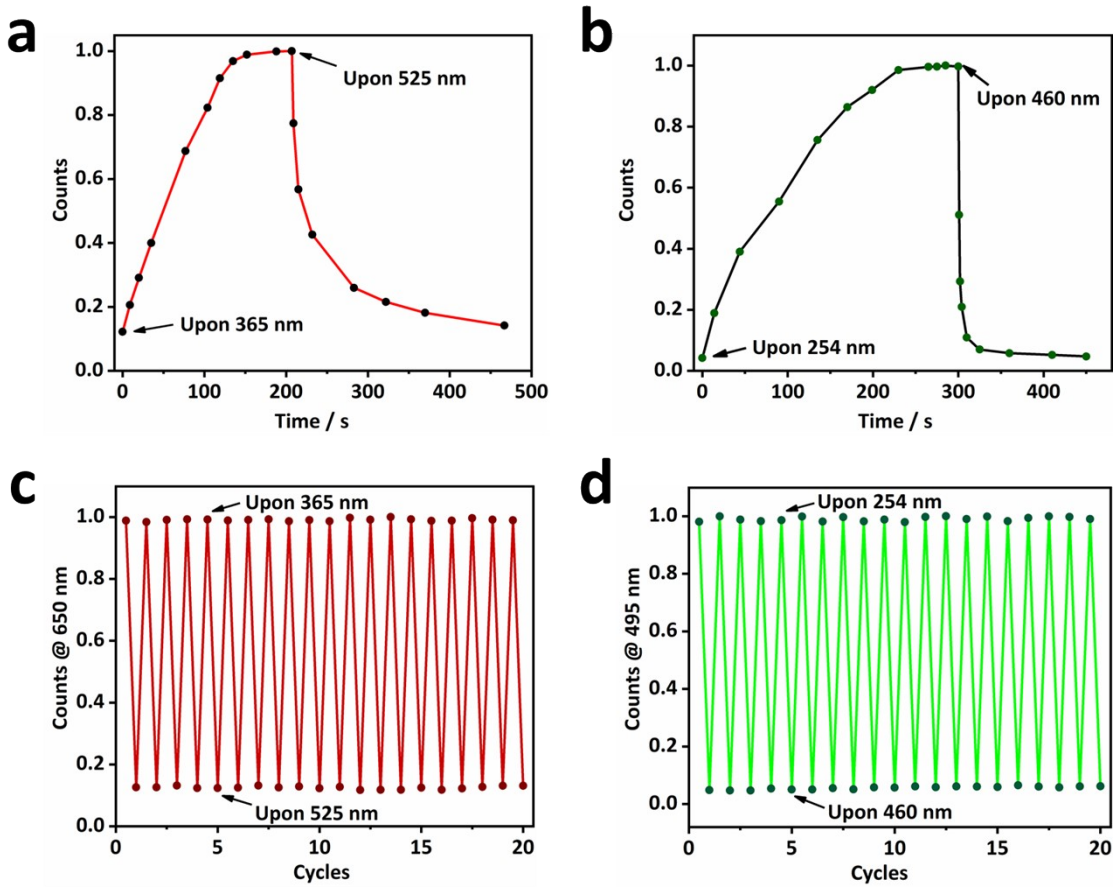

Figure S7. Photoresponsive behaviour of **P1** and **P2**. (a) Fluorescence response of **P1** upon 365 nm UV and 525 nm Vis irradiation. (b) Fluorescence response of **P2** upon 254 nm UV and 460 nm Vis irradiation. (c) Photoinduced switching cycles of **P1** upon alternative irradiation of 365 nm UV for 200 s and 525 nm Vis for 250 s. (d) Photoinduced switching cycles of **P2** upon alternative irradiation of 254 nm UV for 300 s and 460 nm Vis for 150 s. λ_{ex} = 410 nm.

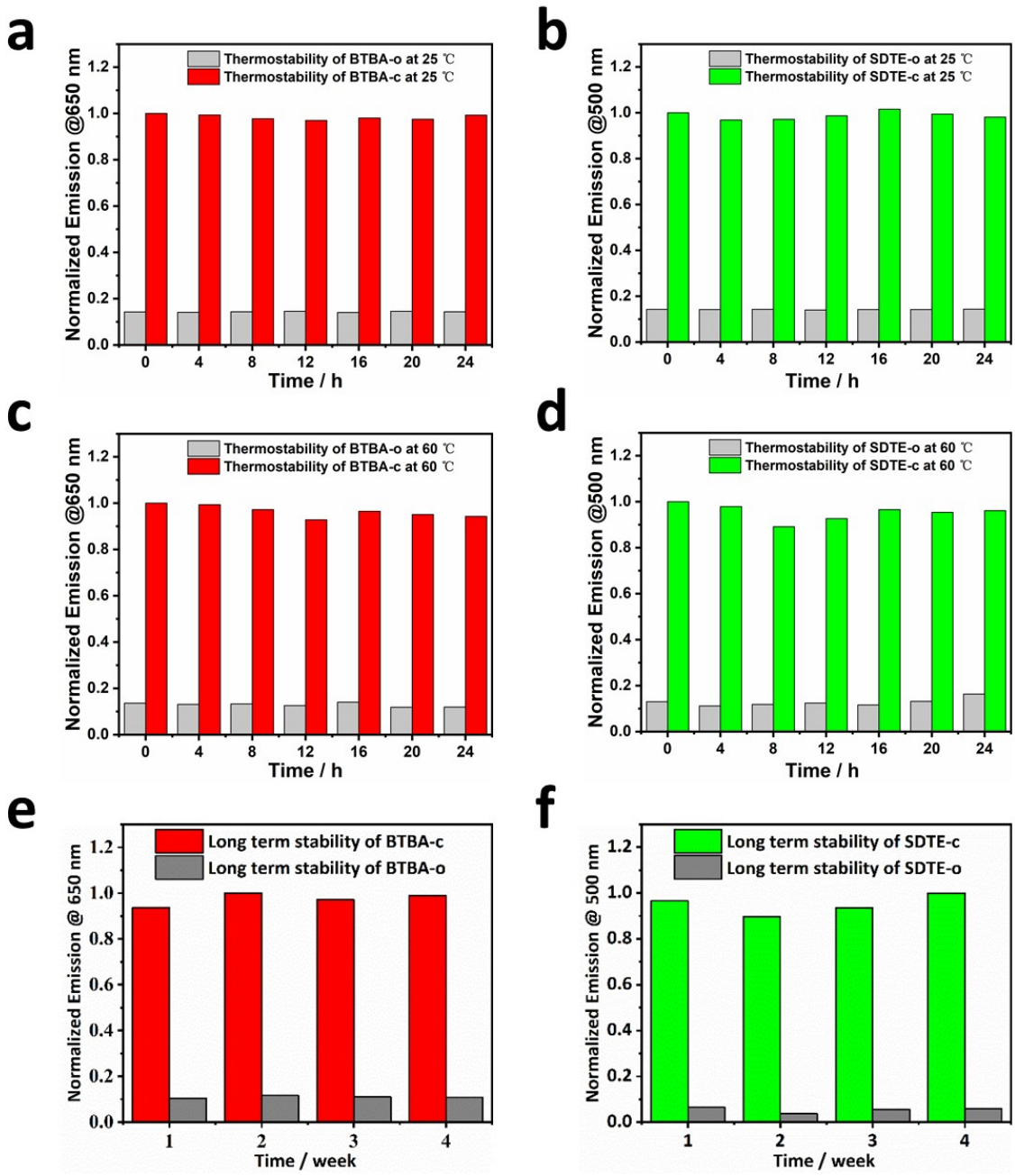

Figure S8. Thermostability of **P1** and **P2**. The thermostability of **P1** (a) and **P2** (b) at 25 °C. The thermostability of **P1** (c) and **P2** (d) at 60 °C. Long-term stability test of **P1** (e) and **P2** (f).

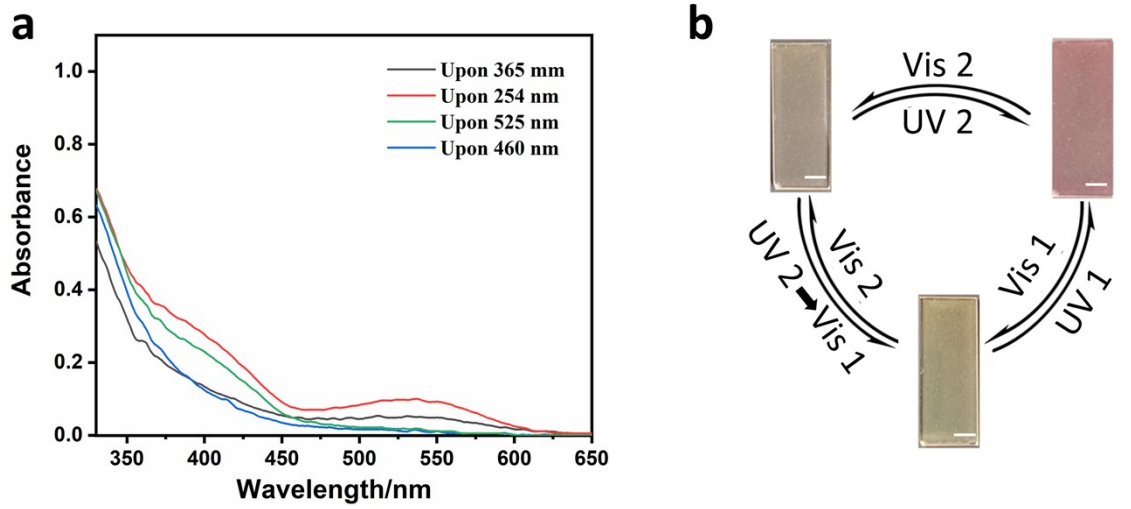

Figure S9. (a) The absorption spectra of **P3** polymer films under illumination of different light (365 nm, 254 nm, 525 nm, and 460 nm). (b) Color change of **P3** polymer film after irradiation with different wavelengths of light. λ_{ex} = 410 nm. All scale bars are 1.0 cm.

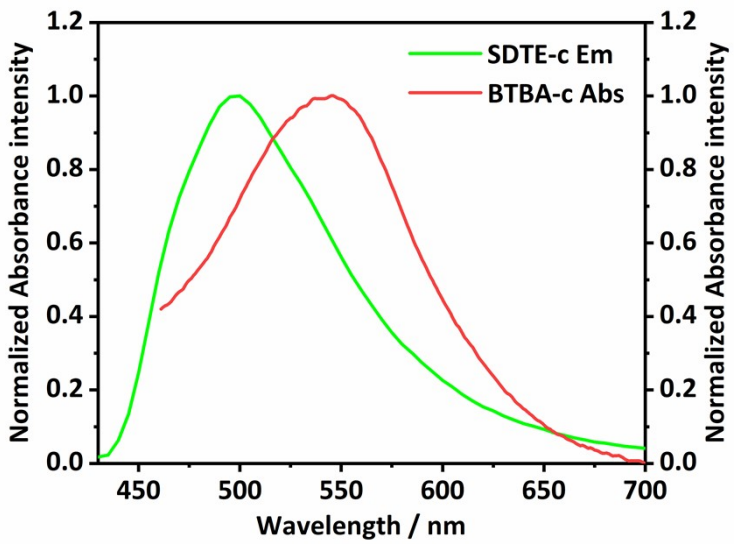

Figure S10. The emission spectrum of SDTE-c units in **P1** and the absorption spectrum of BTBA-c units in **P2**. λ_{ex} = 410 nm.

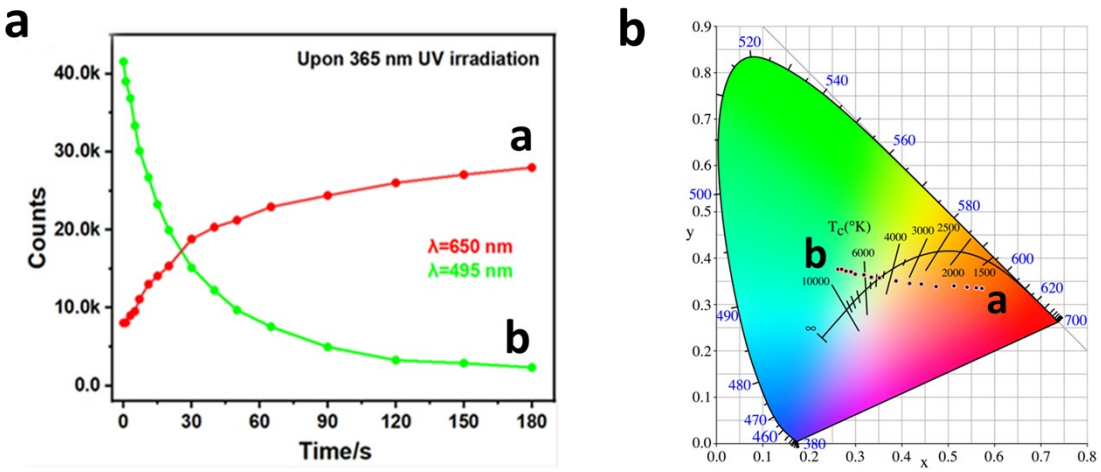

Figure S11. (a) The fluorescen intensity (λ_{max} = 495 nm and λ_{max} = 650 nm) of **P3** using 365 nm UV irradiation for the diferent times. (b) The corresponding CIE coordinate change of the **P3** film. λ_{ex} = 410 nm.

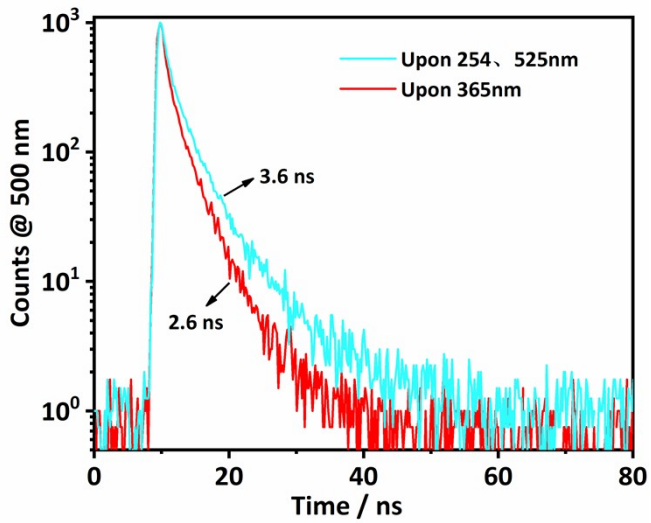

Figure S12. Fluorescence decay curves of P3 upon UV2 (365 nm) (λ_{ex} = 405 nm, λ_{em} = 495 nm).

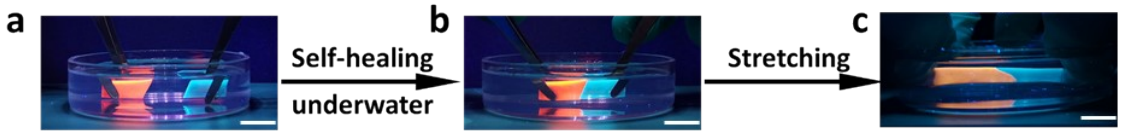

Figure S13. Self-healing of **P1** and **P2** under water, and the photograpgh of the original sample (a), the healed sample before (b), and after stretching (c). All scale bars are 1.0 cm.

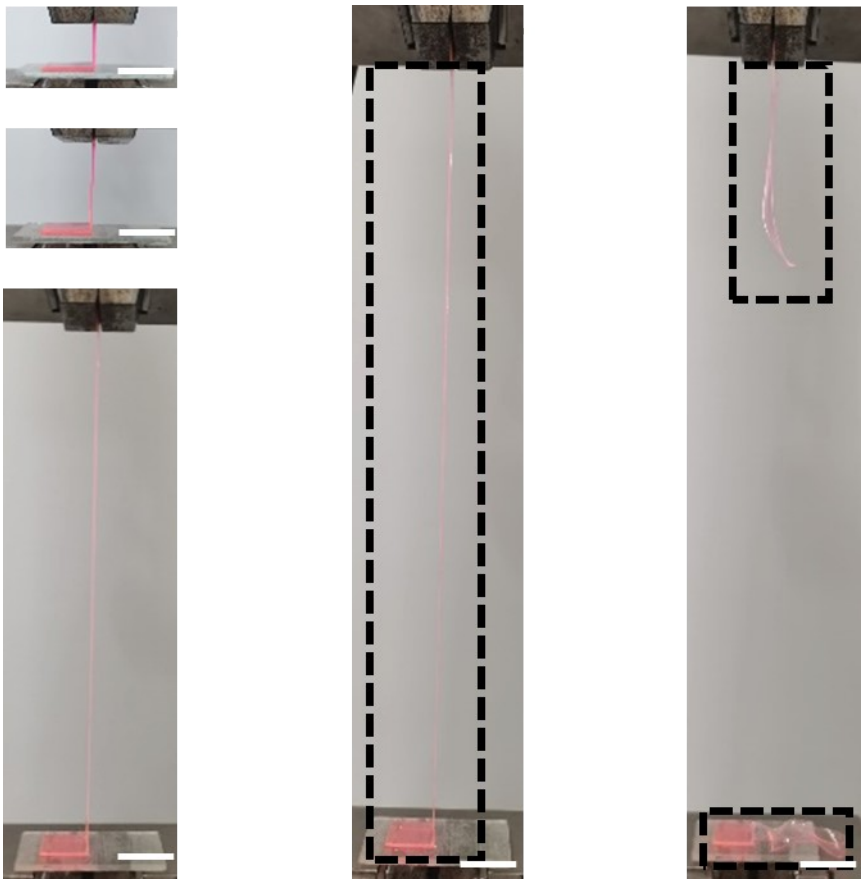

Figure S14. Adhesion test of **P0** sample on glass (Rhodamine B staining) at different stretching states (0% (a), 100% (b), 900% (c), 1500% (d), broken sample (e)). All scale bars are 1.0 cm.

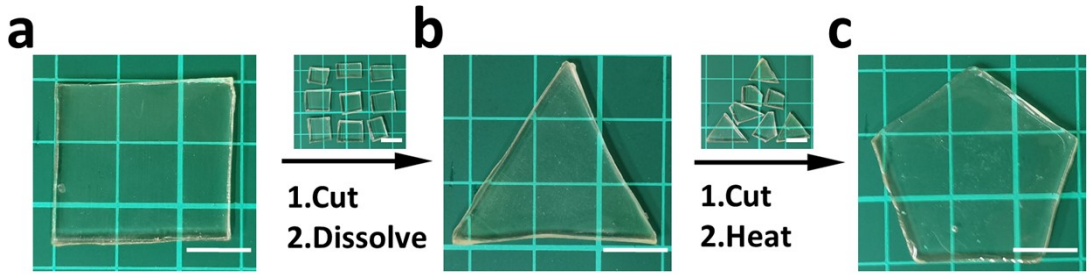

Figure S15. Processability of **P0** using solvent (THF) and heat (100 °C) from a cuboid sample (a) to a triangular body (b) and a pentagonal sample (c). All scale bars are 1.0 cm.

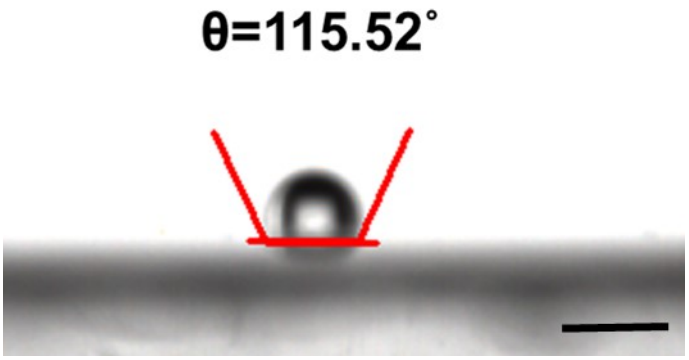

Figure S16. Water contact angle of **P3**. Scale bars=2 mm.

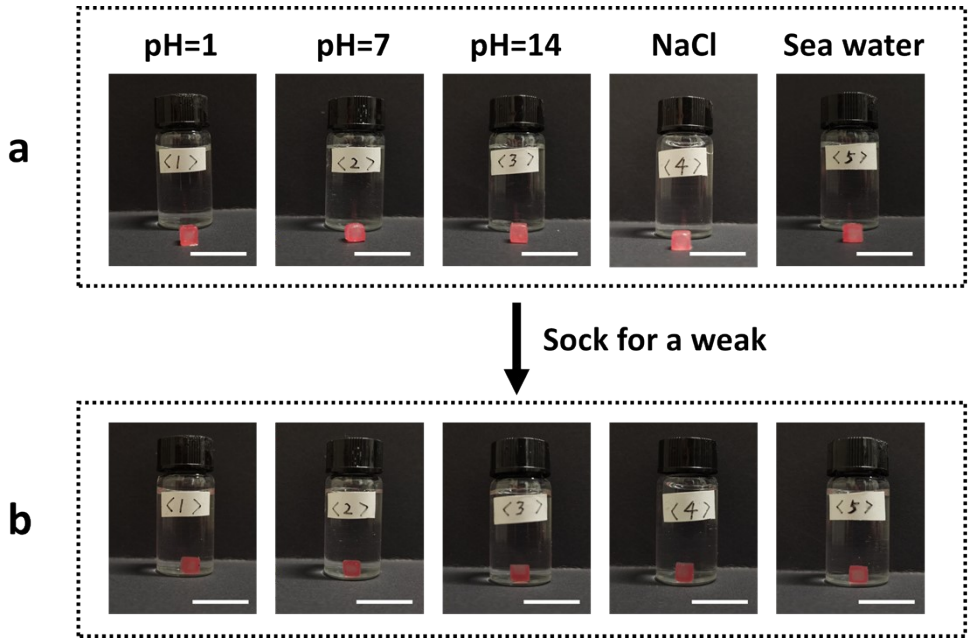

Figure S17. Stability of **P3** in harsh environments (pH=1, pH=7, pH=14, brine (26.5 wt%), seawater) for a week under dark conditions. All scale bars are 1.0 cm.

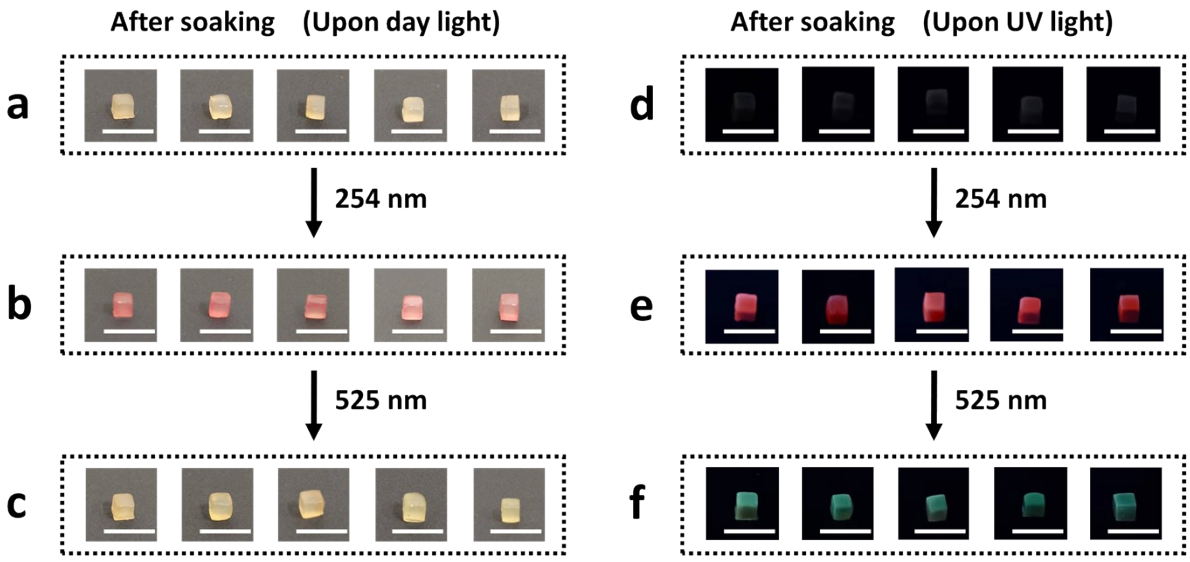

Figure S18. Environmental stability test of **P3** in different soulutions for a week (pH=1, pH=7, pH=14, brine (26.5 wt%), seawater). The color (a, b, c) and fluorescence (d, e, f) change of **P3** in initial state (a,d), 254 UV irradiation (b, e), 525 UV irradiation (c,f). The fluorescence were observed under 365 nm UV light. All scale bars are 1.0 cm.

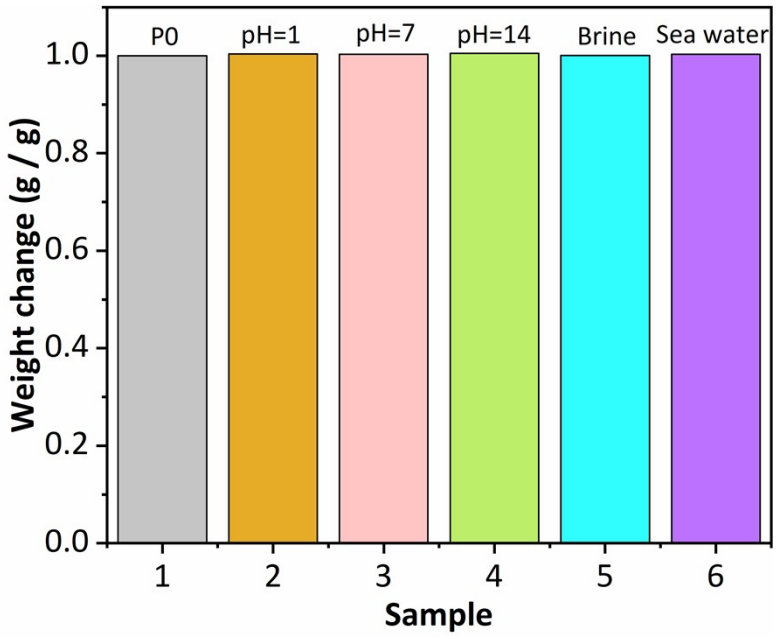

Figure S19. Weight change of **P3** immersed in different soulutions for a week (pH=1, pH=7, pH=14, brine (26.5 wt%), seawater).

Table S2. The fluorescence quantum yields of **P1**, **P2**, and **P3** under ambient conditions and in water.

Sample	P1[a]	P2[a]	P3[a]	
	BTBA-c	SDTE-c	BTBA-c	SDTE-c
ambient conditions	6.35±0.26	3.12±0.12	6.49±0.23	3.36±0.14
water	6.52±0.31	3.08±0.07	6.45±0.28	3.19±0.08

[a] The fluorescence quantum yields of **P1**, **P2**, and **P3** were collected using fluorescence spectrophotometer with integrating sphere (FLS920). SDTE-c: λ_{ex} = 410 nm, λ_{em} = 430-550 nm. BTBA-c: λ_{ex} = 560 nm, λ_{em} = 580-750 nm.

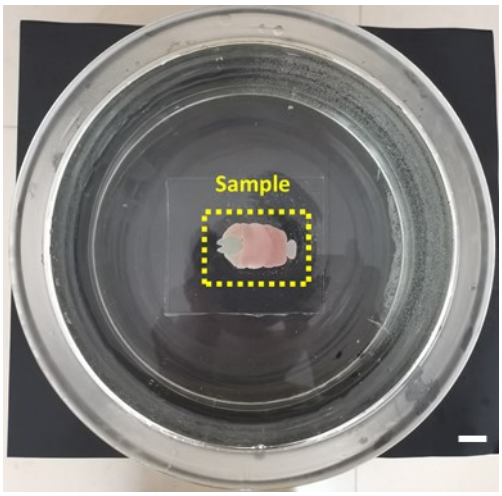

Figure S20. Optical photographs of test device (fish-shaped anti-counterfeiting label). Scale bars=1 cm.

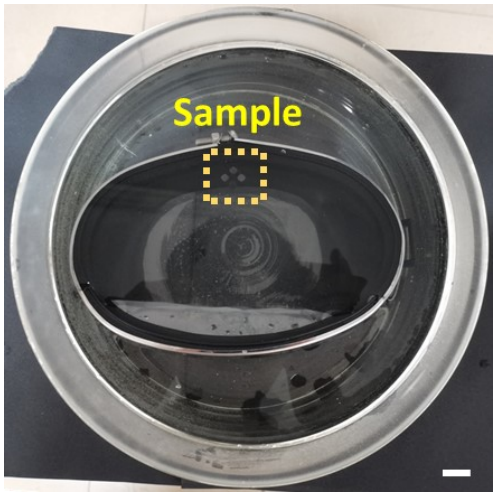

Figure S21. Optical photographs of test device (anti-counterfeiting label in diving goggles). Scale bars=1 cm.

Video S1. Example of a **P0** adhered on glass blocks and the adhesion can resist water blasting. The dimension of the **P0** used for the adhesive exhibition is 10 mm × 10 mm × 1 mm. The water blasting continues for 5 min.

Reference

1. J. Jiang, P. Zhang, Y. Tian, Z. Lin, C. Zhang, J. Cui, J. Chen and X. Chen, *Sci. China Mater.*, 2023, **66**, 1949-1958.