Electronic Supplementary Information

Photothermally triggered one-component shape memory polymer material prepared by cross-linking porphyrin-based amphiphilic copolymer self-assemblies

Yufang Song, ‡ [a] Yiming Chen, ‡ [b] Wangqiu Qian, [a] Dongjian Shi, [a] Weifu Dong, [a] Yang Wang, [a] Piming Ma[*a] and Hongji Zhang[*a]

[a.] Key Laboratory of Synthetic and Biological Colloids, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, China. Email: p.ma@jiangnan.edu.cn; hongjizhang@jiangnan.edu.cn

[b.] Département de chimie, Université de Sherbrooke, Sherbrooke, Québec, J1K 2R1, Canada.

Materials

methyl methacrylate (MMA, AR, Macklin), butyl acrylate (BA, AR, Macklin), acrylic acid (AA, AR, TCI), diacetone acrylamide (DAAM, AR, Macklin), adipic dihydrazide (ADH, AR, Macklin), 2-butoxy ethanol (BCS, AR, Macklin), 5-(4'-Aminophenyl)-10,15,20-triphenylporphyrin (TPP-NH$_2$ 97%, Aladdin), acryloyl chloride (96%, Aladdin), tert-butyl peroxybenzoate (TBPB, AR, Macklin), triethanolamine (AR, Macklin), dichloromethane (HPLC, Macklin), acryloyl chloride (>98%, GC, TCI), petroleum ether (AR, Aladdin), trichloromethane (AR, Sinopharm Chemical ReagentCo., Ltd), methanol (AR, Sinopharm Chemical ReagentCo., Ltd), tetrahydrofuran (THF, HPLC, Macklin), ethanol (HPLC, Macklin), diethyl ether (AR, Sinopharm Chemical ReagentCo., Ltd), N,N-dimethylethanolamine (99%, Macklin) were used without further treatment.

Characterizations

The size of the sample was 75 mm * 25 mm and the thickness was 0.3±0.02 mm. ^{1}H NMR spectra were recorded on a Bruker AVANCE III HD 400 MHz NMR spectrometer (Bruker BioSpin Co., Switzerland) in CDCl$_3$. FTIR examinations were conducted on a Nicolet 6700 FTIR spectrometer. Irradiation was performed by a 655 nm laser (K635E02MN, Changchun New Industries Optoelectronics Technology Co., Ltd., Changchun, China). The temperatures of samples were recorded by infrared thermometer (GasDNA-IR 22). UV-Vis spectra in the wavelength range of 350-850 cm^{-1} were recorded by a Shimadzu UV-3600 plus spectrophotometer with a quartz cuvette. The polymerizing effect of synthesized MBDA-MTPP copolymer was detected by means of gel permeation chromatography (GPC) with reference polystyrene as the calibration standard and THF as the mobile phase (flow rate: 1.0 mL/min). DSC was performed to investigate the T$_g$ of the SMP. The T$_g$ value was obtained from the second heating cycle measuring with a heating rate of 10 ℃/min over the range from 20 to 85 ℃ under a nitrogen atmosphere. The micelle size was investigated by Nano Sizer and Zeta-potential Tester (Bruker ZetaPALS).

Synthesis of N-[4-(10,15,20-Triphenyl-21H,23H-porphin-5-yl) phenyl]-2-propenamide (MTPP)

5-(4'-Aminophenyl)-10,15,20-triphenylporphyrin (TPP-NH$_2$, 500 mg) and triethanolamine (250 mg) were dissolved in 125 mL of dichloromethane. To this solution, acryloyl chloride (250 mg) was added dropwise with stirring for 30 min in an ice bath, then the reaction mixture was stirred at room temperature for 3 h. The solution concentrated by a rotary evaporator until half of its total amount and the solution was filtered to remove impurity. The product was further purified by column chromatography, the eluent was a mixture of dichloromethane and petroleum ether (volume ratio: 1:1). Finally, the pure MTPP was obtained by repeated recrystallization from a mixture of trichloromethane and methanol (volume ratio: 10:1). The synthetic route is shown in Fig. S1. ^{1}H NMR (400 MHz, CDCl$_3$) δ = 8.84 (s, 8H), 8.24 – 8.13

(m, 8H), 7.88 (dd, J = 23.7, 8.2 Hz, 2H), 7.80 – 7.69 (m, 9H), 7.60 – 7.50 (m, 1H), 6.57 (d, J = 16.9 Hz, 1H), 6.34 (dd, J = 16.8, 10.2 Hz, 1H), 5.98 – 5.76 (m, 1H), 2.78 (s, 2H).
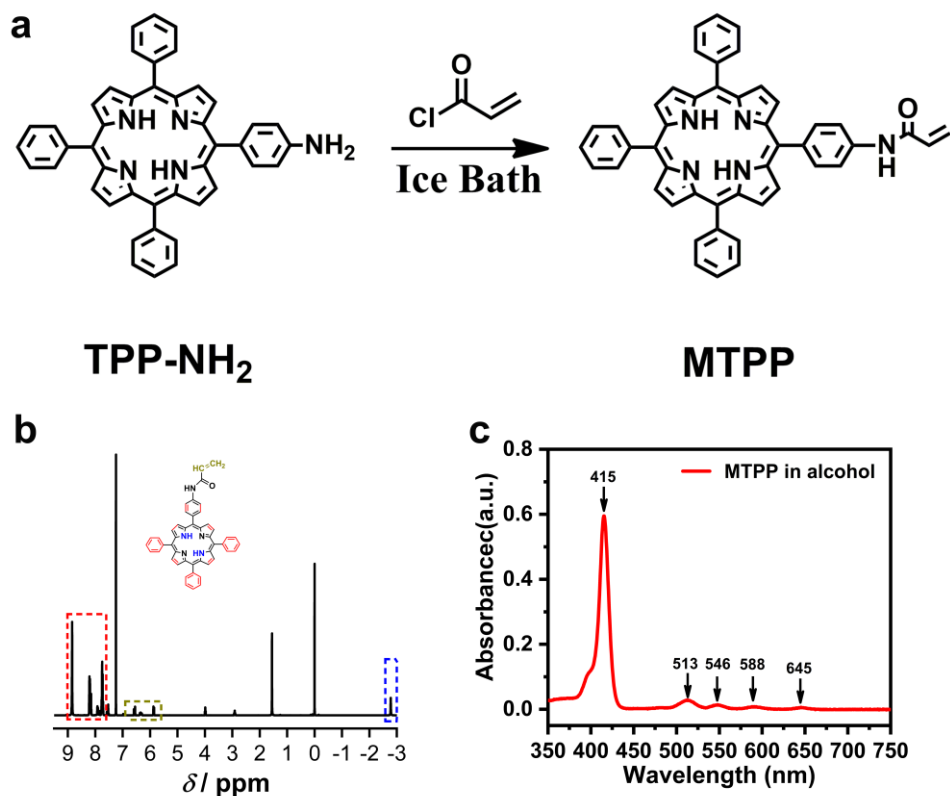
Fig. S1 (a) The synthetic route, (b) ^{1}H NMR spectrum, and (c) UV-vis absorption spectrum (0.001 mg/mL in alcohol) of MTPP.

Preparation of porphyrin-based amphiphilic copolymer MBDA-MTPP

The recipes for preparing amphiphilic copolymers are listed in Tab. S1. The radical copolymerizations were carried out in BCS under nitrogen atmosphere and TBPB was used as the initiator. Taking MBDA-MTPP 0.005% as an example, the synthesis process is described: first, 2-butoxy ethanol (1000 µL) was added to a 50 mL three-necked flask, then heating to 145 ℃ in an oil bath. Second, a mixture of MTPP (2.612 mg), MMA (4.77 mL), BA (3.6 mL), AA (274.4 µL), DAAM (0.406 g) and TBPB (107 µL) was added dropwise into the flask with stirring for 40 min. And the reaction mixture was stirred at 145 ℃ for 4.5 h after addition. The

final product was purified by multiple dissolution–precipitation steps from tetrahydrofuran-diethyl ether to take away the residual monomers, and then dried under vacuum to gain the purificatory MBDA-MTPP copolymer. ^{1}H NMR (400 MHz, CDCl$_3$, δppm): 3.61 (s, -OCH$_3$), 4.00 (t, -OCH$_2$-),6.99 (s, -N-H-). FTIR, 3558 ~ 3065 (overlapped characteristic peak of v_{N-H} and v_{O-H}), 2931 (v_{CH3}), 1732 ($v_{C=O}$), 1609 (δ_{N-H}), 1238 (v_{C-C-O}) and 1142 (v_{C-O-C}).

Tab. S1. The composition of premixed liquid.

Sample	V(MMA)/mL	V(BA)/mL	V(AA)/µL	m(DAAM)/g	m(MTPP)/mg	V(TBPB)/µL	V(BCS)/µL
MTPP 0	4.77	3.6	274.4	0.406	0	107	1000
MTPP 0.005%	4.77	3.6	274.4	0.406	2.612	107	1000
MTPP 0.01%	4.77	3.6	274.4	0.406	5.224	107	1000
MTPP 0.05%	4.77	3.6	274.4	0.406	26.12	107	1000
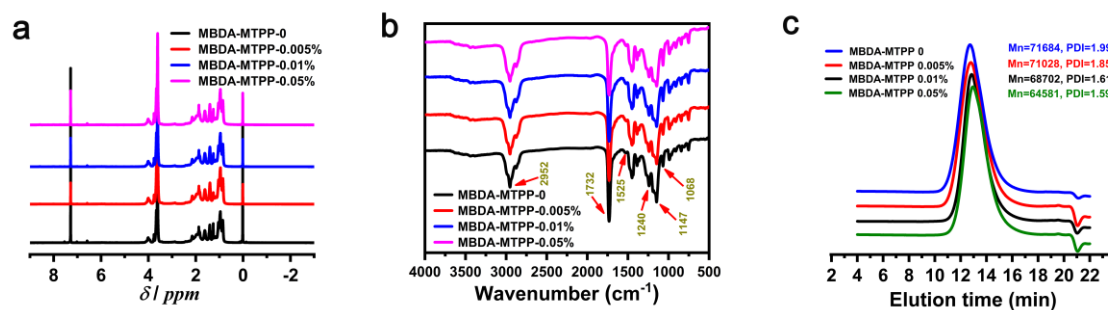
Fig. S2 (a) ^{1}H-NMR spectrum, (b) FTIR spectrum, and (c) GPC curves (in THF) of MBDA-MTPP copolymer.
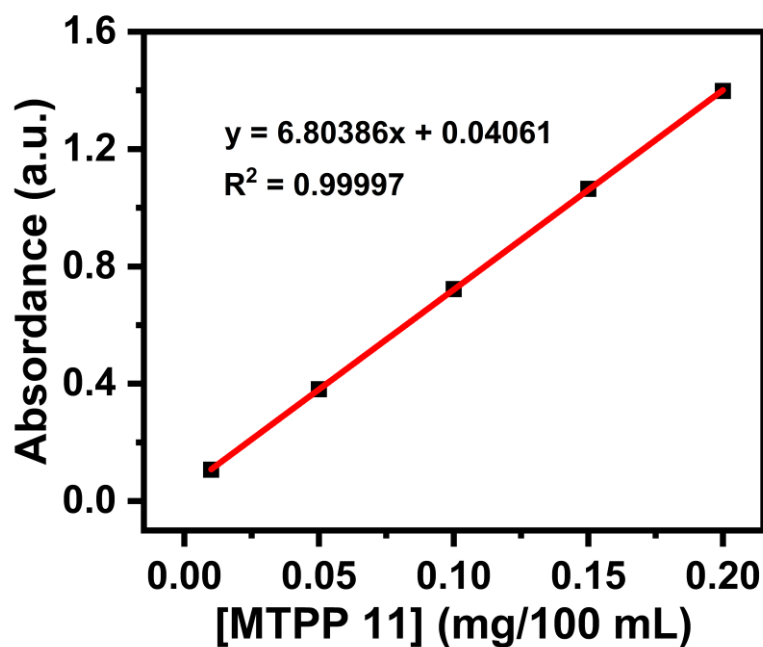
Fig. S3 Standard curve of MTPP concentration and absorption.
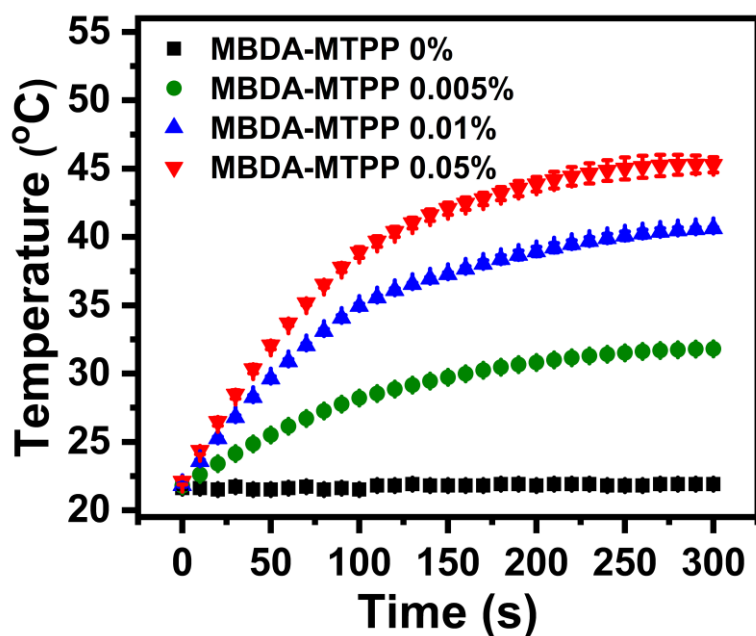

Fig. S4 Light-induced photothermal effect of MBDA-MTPP in ethanol solution: temperature of MBDA-MTPP loaded different contents of MTPP vs. exposure time (λ = 655 nm, 528 mW/cm^2).

**Preparation of porphyrin-based micelles（MBDA-MTPP-NPs）and SMP films（MBDA-**

MTPP-ADH)

MBDA-MTPP amphiphilic copolymers (2 g) with different contents of MTPP were dissolved in 10 mL of THF, respectively. The mixturea were ultrasonicated for 30 min to promote the dissolution of MBDA-MTPP in THF. Preheating the mixtures to 50 ℃ and adjusting the pH of the solutions to 7~8 with N,N-dimethylethanolamine, then deionized water (12 g) was slowly added dropwise into the solutions and keeping stirring for 2 h after addition. THF was evaporated under at 50 ℃ with stirring, then adjusting the solid content of the colloidal solution to 30 wt% with deionized water. Finally, four kinds of polymer micelles MBDA-MTPP 0%-NPs, MBDA-MTPP 0.005%-NPs, MBDA-MTPP 0.01%-NPs, MBDA-MTPP 0.05%-NPs were prepared.

The MBDA-MTPP-NPs were mixed with ADH at a mole ratio of 1:1. Keeping stirring until ADH completely dissolved, then the mixtures were cast on a slick Teflon sheet and dried at room temperature in a dry place for a week, and then the MBDA-MTPP-ADH films were prepared with the volatilization of water molecules. The cross-linking degree of the MBDA-MTPP-ADH films was estimated from the gel content results. For gel fraction (GF), the prepared samples were dried in a vacuum oven until a constant weight (W_1) was obtained. Then, they were weighed again(W_2) after fully immersed in THF for 7 days. The GF was calculated according to: GF (%) = W_2 *100/W_1.
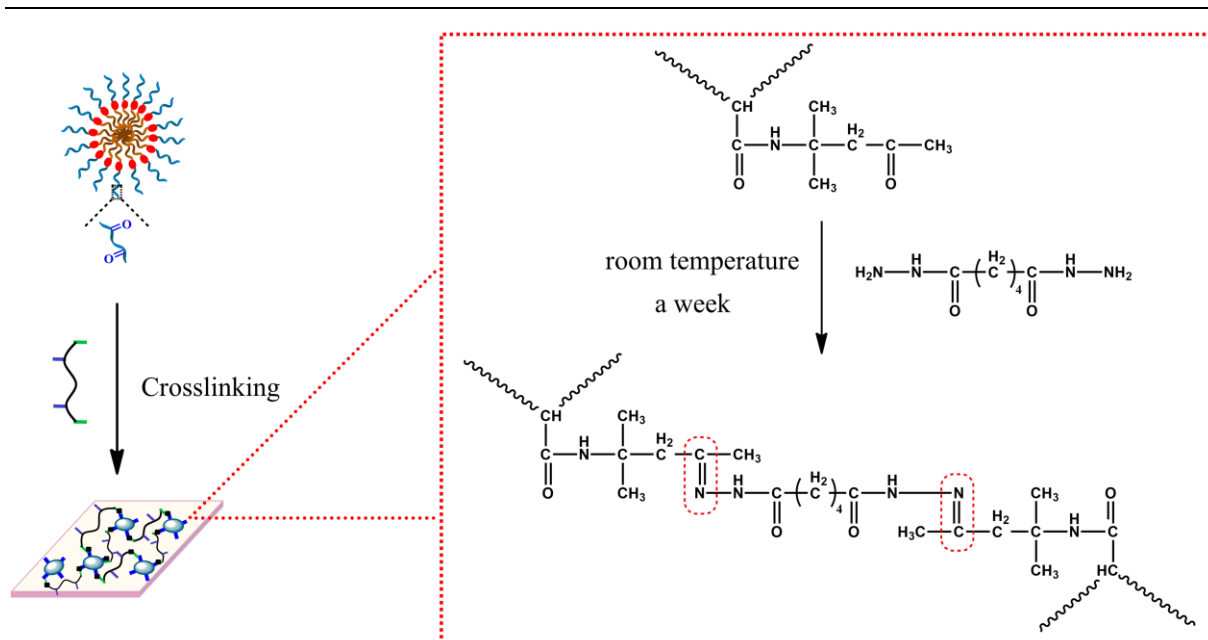
Fig. S5 Crosslinking reaction process of MBDA-MTPP-NPs to obtain films with shape memory effect.
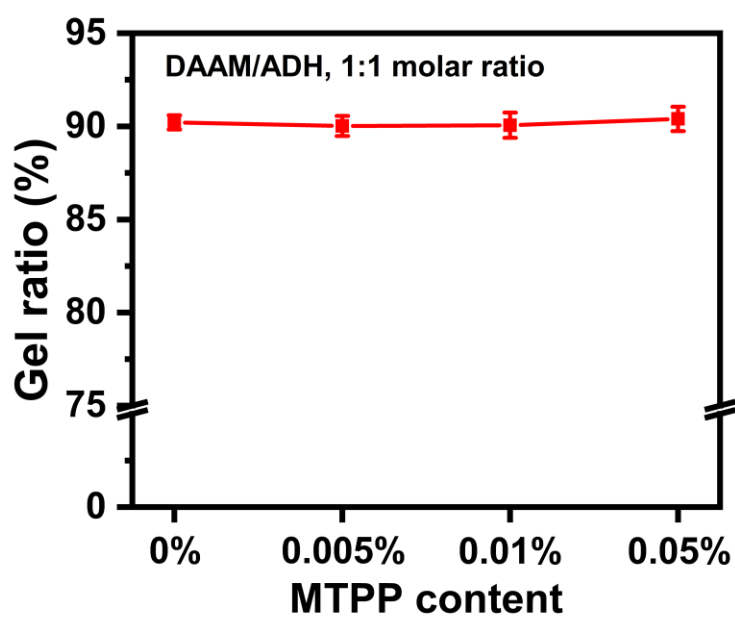
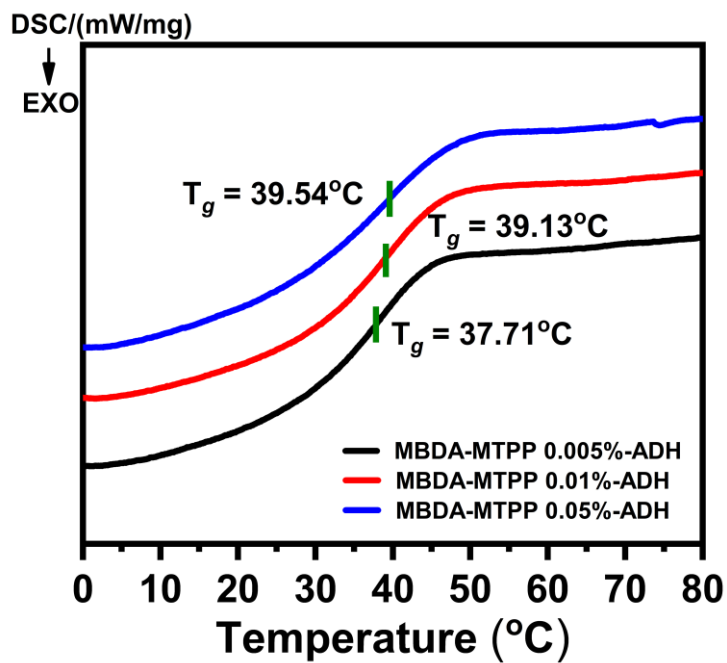**Fig. S6** The gel ratio of MBDA-MTPP-ADH films with different content of MTPP.

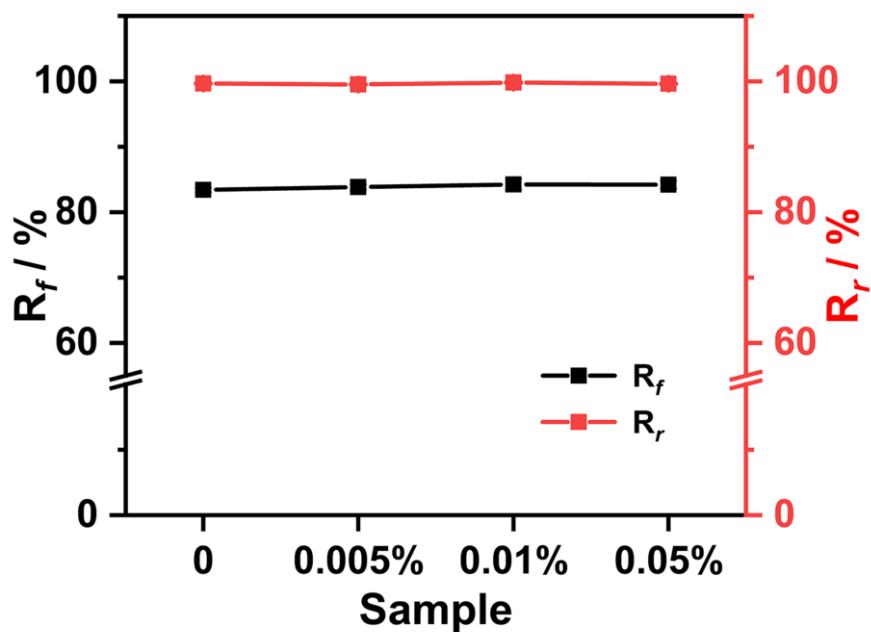**Fig. S7** The glass transition temperature (T_g) of MBDA-MTPP-ADH films were tested by DSC.
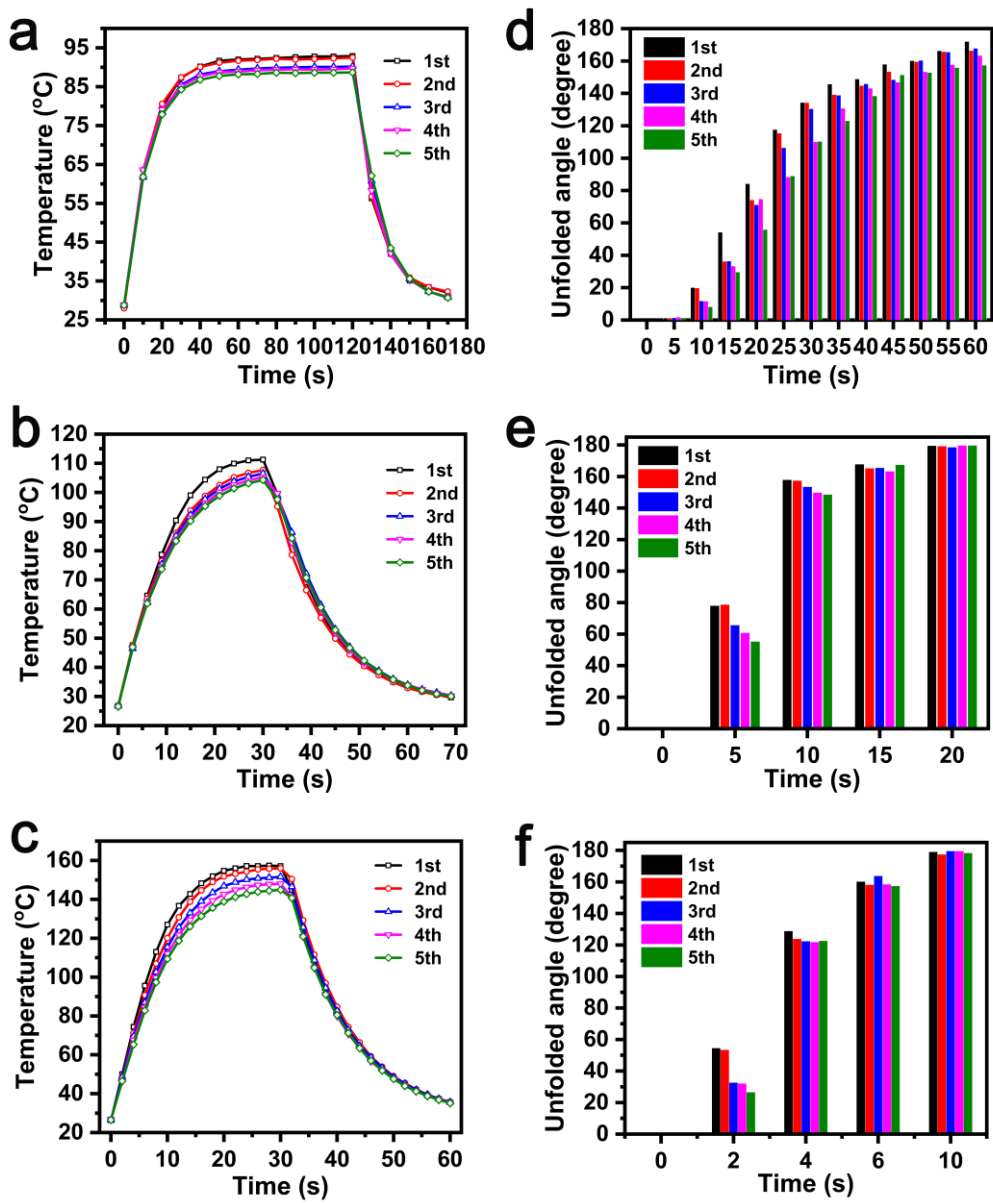

Fig. S8 The shape fixity ratio and shape recovery ratio of MBDA-MTPP-ADH films under thermal stimulation.

Fig. S9 The photothermal stability of MBDA-MTPP-ADH films (a) MTPP-0.005%; (b) MTPP-0.01%; (c) MTPP-0.05%; Shape memory stability of MBDA-MTPP-ADH films (d) MTPP-0.005%; (e) MTPP-0.01%; (f) MTPP-0.05%.