## **Supporting Information**

## Liquid Crystalline Polyurethane Composites Based on Supramolecular Structure with Reversible Bidirectional Shape Memory and Multi-shape Memory Effect

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## Supplementary experimental section

Thermally induced multi-shape memory properties were measured via thermo-mechanical analysis using a TA Instruments DMA800 in controlled-force mode with tension clamps. All samples were cut into rectangular pieces of 10 mm  $\times$  2.0 mm  $\times$  0.5 mm and dried at 100 °C in vacuum for 24 h.

The reversible bidirectional shape memory effect (rbSME) of SMPU-HOBA composites has been investigated through two procedures:

(1) For the visual photographic procedure, standard polymeric strips with 1 mm thickness were synthesized through solution caste route, and then placed at 60 °C oven under 0.1kPa vacuum. After heating to programming temperature (Tform = 90 °C), a ring type shape was formed and fixed at a relatively lower temperature (Tfix = 5 °C), and rbSME was investigated at an intermediate temperature (Trev = 50 °C).

(2) Quantitative rbSME were studied with standard rectangular pieces of dimension  $(30 \times 10 \times 1)$  mm3 using a TA Instruments DMA800 in controlled-force mode. Parameters of elongation experiments:  $\epsilon$ prog = 20%, Tform = 90 °C, Trev = 50 °C, Tfix = 0 °C. After programming, a shape A was formed as  $\epsilon$ A at Tform. Then cooling to Tfix at a rate of 4 °C min<sup>-1</sup>, shape B was obtained, marked as  $\epsilon$ B. After that, reheating to Trev at a rate of 4 °C min<sup>-1</sup> and allowed to equilibrate for 1 min.

Supplementary tables and figures

 Table S1 Composition of SMPU-HOBA composites

Samples	Mass (g)			HOBA
		HOBA	R <sup>a</sup>	content
				(wt%)
Pure SMPU	10.0	0	0	0
SMPU-0.2HOBA	10.0	0.79	0.2	7.3
SMPU-0.4HOBA	10.0	1.56	0.4	13.5
SMPU-0.6HOBA	10.0	2.36	0.6	19.1
SMPU-0.8HOBA	10.0	3.13	0.8	23.8
SMPU-1.0HOBA	10.0	3.93	1.0	28.2

<sup>a</sup> R: Molar ratio of ([C=O] in HOBA)/([N–H] in BINA)



**Figure S1.** WAXD patterns of the samples (a) HOBA, SMPU, SMPU-0.2HOBA and SMPU-1.0HOBA; (b) SMPU and SMPU-HOBA composites with various HOBA contents.



Figure S2. TG–DTG curves of the samples: a-TG curves, b-DTG curves.





Figure S4. POM images of HOBA at different temperature: (a) 115 °C, (b) 165 °C. (×400)

